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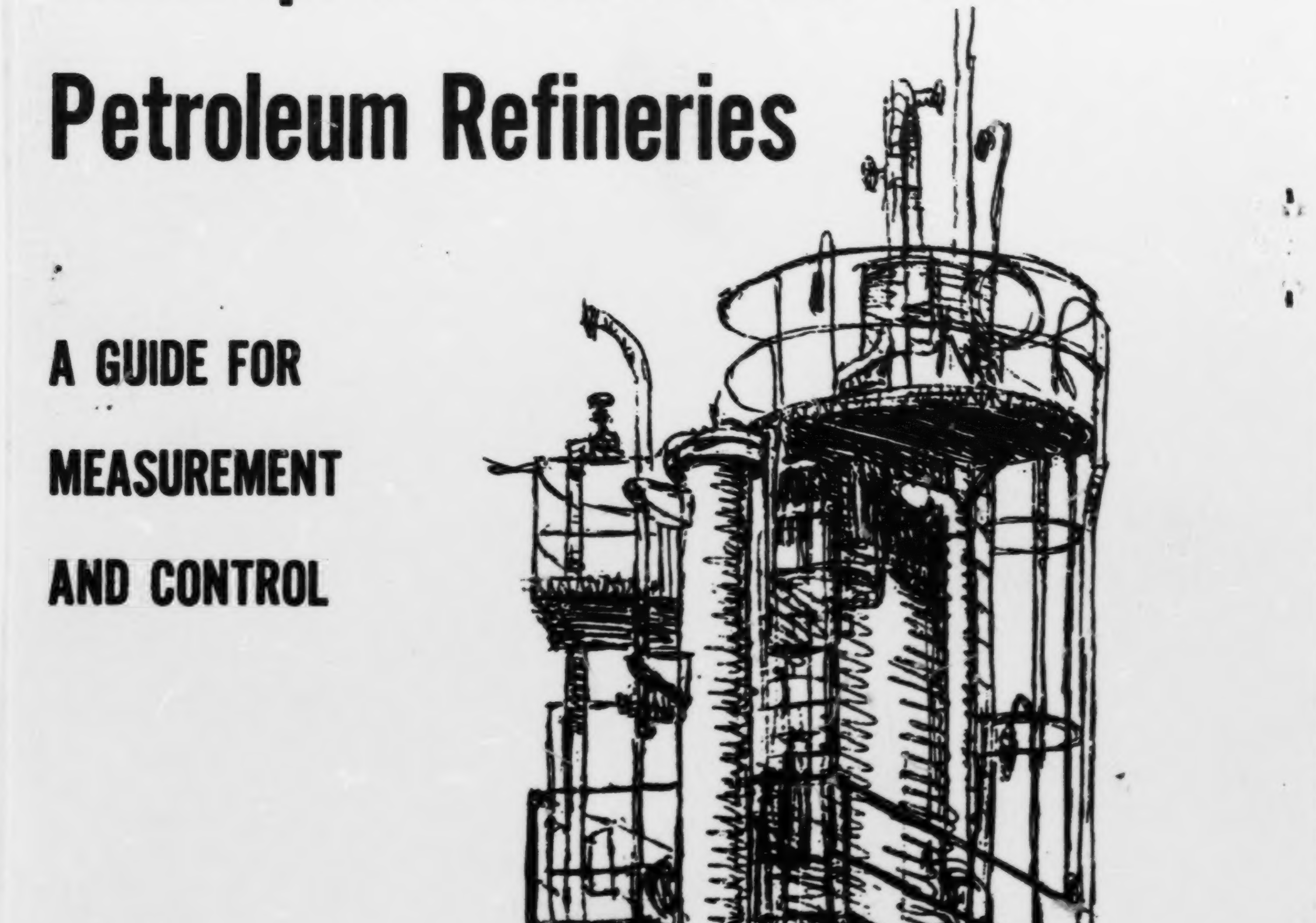
Atmospheric Emissions from Petroleum Refineries

A GUIDE FOR MEASUREMENT AND CONTROL



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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

Atmospheric Emissions from Petroleum Refineries

A Guide for Measurement and Control

U.S. DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
Public Health Service • Division of Air Pollution

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Foreword

In September 1955 a study, known as the "Joint Project," was started to determine the quantity and nature of emissions from oil refineries located in Los Angeles County. At that time there were 18 refineries in Los Angeles County with a combined capacity of over 700,000 barrels of crude oil per day. These refineries are located in or near the city of Los Angeles, often adjacent to commercial or residential areas.

The following agencies participated in the Joint Project: Los Angeles County Air Pollution Control District; U.S. Department of Health, Education, and Welfare, Public Health Service, Air Pollution Engineering Research; State of California, Department of Public Health, Bureau of Air Sanitation; and representing the oil industry, the Western Oil and Gas Association, Air Pollution Control Committee. Formally titled the "Joint District, Federal and State Project for the Evaluation of Refinery Emissions," the Joint Project took about 3 years to complete and was designed to be the first comprehensive field study of atmospheric emissions from oil refineries. The program to obtain this objective included:

1. A study of all refinery operations with respect to equipment, products, operating conditions, and points of possible emissions to the atmosphere.
2. Development or adaptation of sampling and analytical methods.
3. Field testing.
4. Evaluation, classification, and extrapolation of test results to the total petroleum refining industry in Los Angeles County.

The work of the Joint Project has been presented in nine reports published by the Los Angeles County Air Pollution Control District in behalf of the collaborating agencies. These reports are collectively titled: Joint District, Federal and State Project for the Evaluation of Refinery Emissions. (Los Angeles County Air Pollution Control District, 434 South San Pedro Street, Los Angeles 13, Calif.) The individual titles are:

a. Kanter, C. V., et al., "Interim Progress Report" (July 1956).
b. Palmer, R. K., "Hydrocarbon Losses from Valves and Flanges," Report No. 2 (March 1957).

c. Steigerwald, B. J., "Hydrocarbon Leakage from Pressure Relief Valves," Report No. 3 (May 1957).

d. Sussman, V. H., "Atmospheric Emissions from Catalytic Cracking Unit Regenerator Stacks," Report No. 4 (June 1957).

e. Bonamassa, F., "Emissions of Hydrocarbons to the Atmosphere from Cooling Towers," Report No. 5 (August 1957).

f. Steigerwald, B. J., "Emissions of Hydrocarbons from Seals on Pumps and Compressors," Report No. 6 (December 1957).

g. DeVorkin, H., Steigerwald, B. J., "Emissions to the Atmosphere from Boilers and Process Heaters," Report No. 7 (May 1958).

h. Kanter, C. V., et al., "Emissions to the Atmosphere from Eight Miscellaneous Sources in Oil Refineries," Report No. 8 (June 1958).

i. Kanter, C. V., et al., "Emissions of Air Contaminants from Oil Refineries," Final Report (June 1958).

For each source studied these reports detail sampling and analytical techniques, results of field testing programs, data evaluation techniques, and total emissions from the refineries in Los Angeles County.

This manual supplements the Joint Project reports and stresses the use which can be made of the methodology and results of the Joint Project in estimating emissions from refineries. It also includes a discussion of equipment and processes, and details on the sources, magnitude of emissions, and methods of control in effect in Los Angeles County refineries.

It is designed to be of use to three groups of people:

(1) Persons not technically trained in either air pollution control or petroleum refining technology who need some understanding of refinery emissions to the atmosphere and their control;

(2) Persons trained in air pollution control who need a better understanding of petroleum refining technology;

(3) Persons trained in petroleum refining technology who need a better understanding of air pollution control.

ARTHUR C. STERN, *Chief*
Air Pollution Engineering Research
Robert A. Taft Sanitary Engineering Center.

Acknowledgments

The reports cited in the bibliography list the names of the many people who provided the test methods and data without which this manual could not have been prepared. The manual was principally prepared by Bernard J. Steigerwald (while he was with the Public Health Service prior to joining the faculty of Case Institute of Technology, Cleveland, Ohio) and Andrew H. Rose, Jr., Chief, Engineering Research & Development Unit, Air Pollution Engineering Research, Robert A. Taft Sanitary Engineering Center. The assistance of the American Petroleum Institute and the air pollution control agencies of Los Angeles County and the Bay Area, California, and of Philadelphia, Pa., in critically reviewing the several drafts of this manuscript is gratefully acknowledged.

Introduction

The Engineers Joint Council has defined air pollution as "the presence in the outdoor atmosphere of one or more contaminants, such as dust, fumes, gas mist, odor, smoke or vapors in quantities, of characteristics, and of duration, such as to be injurious to human, plant, or animal life or to property, or which unreasonably interfere with the comfortable enjoyment of life or property."

The assessment of potential sources of contaminants from a modern oil refinery which may contribute to air pollution is a difficult job because of the complexity of the refining process, the unique nature of any one refinery, the large number and wide distribution of possible sources, the variety of emissions, the inaccessibility of some sources, and difficulties in the identification of some emissions. The processes and equipment in a refinery depend on the age of the refinery, the types of the crude oil used, and the products manufactured. Nearly all refineries have many possible emission sources, ranging from stacks on combustion units to pipeline flanges. Some of these emissions will not be visible; many will be odorless.

With the general acceptance of the theory that certain hydrocarbons, innocuous in themselves, can react photochemically in the atmosphere to produce characteristic smog or air pollution manifestations (1), there has been special interest in those activities and operations which emit hydrocarbons. Because of the nature of the processes involved and the type of materials handled, the refining of petroleum may be an important source of hydrocarbon emission.

The evaluation of these hydrocarbon emissions presents a particularly difficult problem. Due to the chemical characteristics of hydrocarbons, the usual equipment and techniques used for air analyses are not effective for sampling and determining hydrocarbon emissions.

Petroleum hydrocarbons vary from light, highly volatile materials to heavy, nonvolatile residues. Only a few of these hydrocarbons participate to any great extent in the chemical reactions leading to air pollution manifestations. In this manual no attempt has been made to differentiate between hydrocarbons which are known to be active in smog formation and those which are nonreactive. Hydrocarbon emissions cited herein are based on total hydrocarbons without respect to type. Unsaturated hydrocarbons are presently believed to be the ones most active in smog formation. Unsaturated hydrocarbons constitute only a fraction of the total hydrocarbon emissions from petroleum refining.

Petroleum Refining

The petroleum industry can logically be divided into three major divisions: production, refining, and marketing. Production includes the operations involved in locating and drilling oil fields, removing oil from the ground, pretreatment at the well site, and transporting the crude to the refinery. The extent of pretreatment depends on the type of crude oil, and usually includes removal of gas and brine. Refining is limited to the operations necessary to convert the crude into salable products. Marketing involves the distribution and sale of the finished petroleum products. All of these activities may be sources of emissions to the air. Emissions from the marketing of petroleum products will generally be limited to hydrocarbons which escape during filling operations and product storage, while production and refining may be the sources of many types of emissions from the complex equipment and operations involved. This manual is limited to the discussion of atmospheric emissions from petroleum refining.

Some knowledge and understanding of the equipment and processes of petroleum refining are necessary to make a reliable survey of emissions to the atmosphere from petroleum refineries. Detailed information concerning capacities, type of equipment, and control measures is necessary and usually can be obtained through conferences with refinery personnel, inspection of plant flowsheets, and trips through the refinery. Detailed descriptions and flowsheets for all commercial processes, and information on the capacities of the various processes for each refinery in the country are also available from the literature (3)(4).

Oil refining began about 100 years ago with the separation of kerosine from crude oil in simple batch stills. Demand for gasoline, fuel oils, lubricating oils, solvents, asphalt, petrochemicals, and other petroleum products soon developed. To supply these needs, plants were built to separate more effectively the crude oil, crack or split heavy hydrocarbon molecules, polymerize or join light gaseous hydrocarbons, rearrange the internal structure of hydrocarbon molecules, and effectively remove impurities. The modern oil refinery is a complex array of equipment and processes, and mirrors present demands for a wide variety of high quality products.

Future changes in refinery technology will occur to meet developing needs. A few of the factors which might influence future changes

Location and Capacities as of January 1, 1960

[illegible]	[illegible]	*	**	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Alabama	4	15,850	18,400	10,350										10,100
Arkansas	6	84,940	88,410	45,400	13,000	32,700	8,500	16,740	22,500	3,500	2,300	4,600	400	9,090
California	37	1,341,095	1,408,448	551,785	523,395	364,455	122,600	234,905	221,445	49,535	3,980	22,970	3,580	67,170
Colorado	7	37,100	41,800	5,200	13,200	11,300	5,300	7,650			1,300			1,200
Delaware	2	143,500	153,685	92,540	42,000	58,000	44,000	45,000	88,000	5,000	5,100		1,200	1,665
Florida	1	2,000	2,200		......	......	......	......	......					1,100
Georgia	1	7,000	8,000				......							5,000
Illinois	13	598,500	627,050	175,780	121,055	267,470	60,640	148,645	162,275	31,145	10,410	4,800	1,880	34,655
Indiana	12	489,100	523,850	182,200	138,000	168,150	23,100	116,100	96,400	15,160	3,750	10,250	1,865	21,500
Kansas	13	331,600	351,005	86,200	60,300	126,500	61,800	71,300	28,800	20,400	4,700	3,600	990	21,050
Kentucky	4	103,000	110,550	32,000	10,500	36,400	15,200	9,000	12,500		4,400			12,000
Louisiana	12	777,610	810,000	225,315	113,000	331,600	159,100	134,250	31,400	52,700	12,215	12,130	325	13,485
Maryland	3	30,000	36,500	18,500										20,600
Massachusetts	1	50,000	55,000	13,100		20,000	15,000	7,200	7,200		1,800			10,000
Michigan	14	171,900	184,560	56,500	23,700	64,200	15,000	27,750	33,350	5,550	2,950		350	13,300
Minnesota	4	66,785	69,500	10,000	12,000	26,000	15,000	7,800	18,900		1,970		600	5,000
Mississippi	3	16,200	18,500	2,500	4,800	9,300	16,300	2,500	1,200	2,500			225	3,200
Missouri	1	76,100	78,500	7,200	29,400	35,500	2,000	14,000	20,000	3,800	2,200		400	3,000
Montana	10	85,515	95,820	26,000	19,705	31,200	20,500	11,250	39,800	2,300	5,155		200	14,975
Nebraska	1	2,800	3,000		1,100			650		......				
New Jersey	8	573,050	604,740	231,115	63,725	181,440	31,000	80,135	157,290	18,155	6,780	8,000	800	24,600
New Mexico	5	27,980	29,900	5,900	1,875	8,850	3,900	3,950	2,500	2,000				2,100
New York	3	89,000	93,050	21,300		47,240	12,500	16,400	18,900	3,000	3,200			5,300
North Dakota	2	43,200	46,000		1,000	18,000	7,000	6,700		1,800	1,440			
Ohio	11	425,720	454,920	87,200	84,560	207,390	86,000	86,835	59,500	12,455	13,205	3,600	790	20,200
Oklahoma	14	406,600	425,505	121,330	88,255	163,765	64,600	72,770	61,390	18,455	9,065	11,150	1,185	10,500
Oregon	1	3,800	7,000	7,000			......							4,500
Pennsylvania	13	670,300	707,050	221,600	129,590	248,780	62,660	165,455	178,015	20,580	8,245	28,645		10,225
Rhode Island	2	14,700	15,475	1,840		......	......	......	......					8,665
South Carolina	1	11,440	13,000	10,500					......					5,949
Tennessee	1	18,500	20,000	6,500		7,000	2,000			1,200	500			3,000
Texas	57	2,561,920	2,714,535	840,215	458,820	974,195	220,385	543,205	576,690	122,545	28,045	70,380	515	45,100
Utah	5	99,700	103,110	30,000	8,500	37,900	11,500	16,100	1,000	5,000	1,100			2,850
Virginia	1	36,800	38,000	21,000	14,000	22,000	9,000	7,600	22,600		2,500		700	
Washington	6	152,500	164,370	59,945	8,900	67,575	20,700	29,945	41,890	6,355	6,720			7,700
West Virginia	2	6,870	7,000	2,000	2,150			2,500	2,500		155	1,600		
Wisconsin	2	19,250	20,500	7,000	1,500			3,300	5,200					3,700
Wyoming	9	107,950	117,395	42,875	21,445	46,235	4,600	15,745	20,245	2,590	2,285	840	193	12,065
Puerto Rico	2	89,400	94,500	59,200	20,000	42,500	23,600	7,460	10,000	1,700	2,830			
Total	294	9,789,355	10,360,868	3,317,090	2,029,555	3,655,645	1,143,565	1,912,840	1,941,390	407,425	148,300	182,565	16,198	434,544

* Barrels Per Calendar Day. ** Barrels Per Stream Day.

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TABLE 1. *Survey of refineries in United States*

include rapid growth in the use of petrochemicals, a shift in emphasis from the fuel requirements of internal combustion engines to those of jet aircraft and possibly automobile turbine engines, the development of power from nuclear and solar sources, and the use of coal, oil shale, and less desirable crudes as refinery raw material.

At the present time there are over 300 refineries distributed throughout the United States with a combined crude oil capacity of about 10 million barrels per day (table 1). Predictions indicate a continued rapid growth pattern, with a domestic demand for petroleum products in 1965 of almost 13 million barrels per day. It is anticipated that refinery expansion costing $11.4 billion will be necessary to meet this demand (5).

Although a modern refinery is a complex integration of many processes and appears to be a maze of pipelines, valves, pumps, towers, and vessels, the entire operation can be conveniently discussed in terms of four major steps—separation, conversion, treating, and blending. The crude oil is first separated into selected fractions; the relative volume of each fraction (e.g., gasoline, kerosine, fuel oil, etc.) is determined by the type of crude oil used. Since the relative volumes of each fraction produced by merely separating the crude may not conform to the relative demand for each fraction, some of the less valuable separation products are converted to products with a greater sale value (e.g., heavy naphtha to gasoline) by splitting, uniting, or rearranging the original molecules. The products from both the separation and conversion steps are treated, usually by the removal or inhibition of gum-forming materials. As a final step, the refined base stocks are usually blended with each other and various additives to meet product specifications and to arrive at the most valuable and salable combination of products.

Although petroleum refining may be discussed generally in terms of the unit processes of separation, conversion, treating, and blending, each refinery is unique in design and no two will have exactly the same processing scheme. Some refineries employ minimum processing, limited to crude topping or skimming and simple treating (fig. 1); other intermediate refineries practice crude skimming, limited cracking, treating, and some manufacture of heavy products such as lube oil, grease, and coke (fig. 2); many large refineries practice complete refining, including crude topping, catalytic cracking, light hydrocarbon processing such as polymerization or alkylation, manufacture of lube oils, greases, asphalts, and waxes, and usually catalytic reforming or isomerization to improve gasoline quality (fig. 3).

The following sections include general information on the processes and equipment used in oil refineries to manufacture petroleum products.

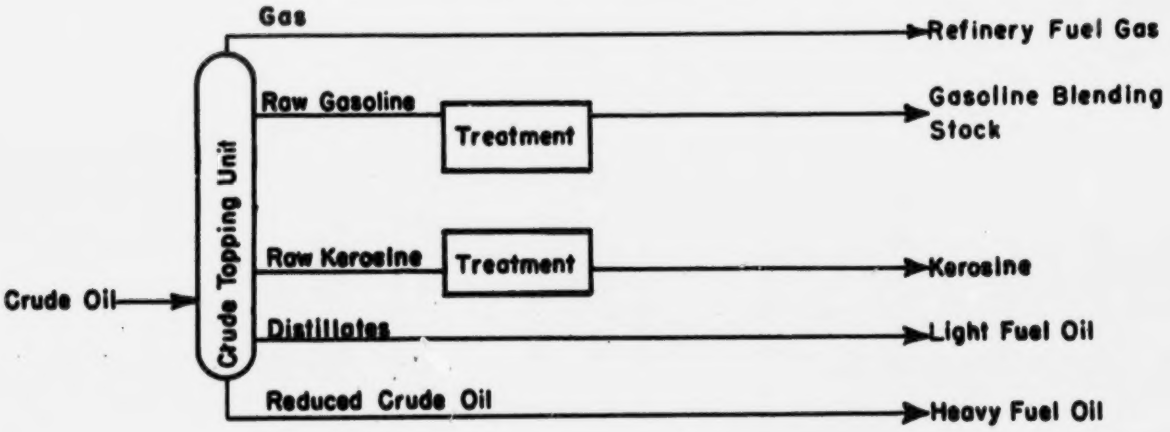
Gas
Refinery Fuel Gas
Raw Gasoline
Treatment
Gasoline Blending Stock
Crude Topping Unit
Raw Kerosine
Treatment
Kerosine
Crude Oil
Distillates
Light Fuel Oil
Reduced Crude Oil
Heavy Fuel Oil

FIGURE 1. *Processing plan for minimum refinery*

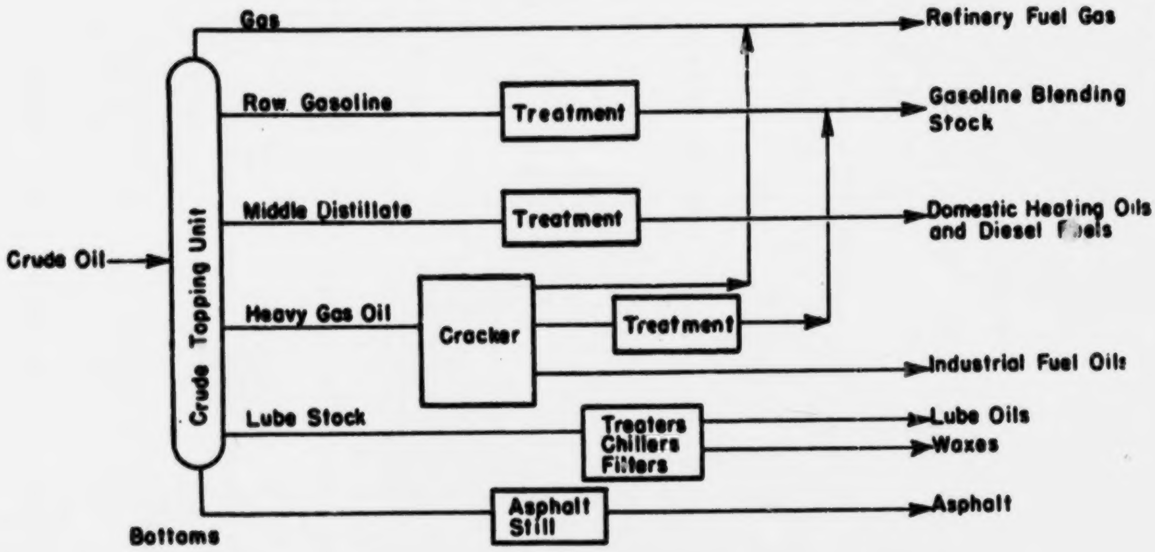
Gas
Refinery Fuel Gas
Raw Gasoline
Treatment
Gasoline Blending Stock
Middle Distillate
Treatment
Domestic Heating Oils and Diesel Fuels
Crude Oil
Crude Topping Unit
Heavy Gas Oil
Cracker
Treatment
Industrial Fuel Oils
Lube Stock
Treaters Chillers Filters
Lube Oils
Waxes
Asphalt Still
Asphalt
Bottoms

FIGURE 2. *Processing plan for intermediate refinery*

Crude Oil Distillation

Crude oil is a mixture of many different hydrocarbons, some of them combined with small amounts of impurities. Crudes vary in appearance from dense black semisolids resembling tar to light, almost colorless fluids. Crudes vary considerably in composition and physical properties, and usually consist of three families of hydrocarbons: paraffins—saturated hydrocarbons having the empirical formula C_nH_{2n+2}; naphthenes—ring-structure saturated hydrocarbons having the empirical formula C_nH_{2n}; and aromatics—characterized by having a benzene ring, C_6H_6, in the molecular structure. Significant elements other than carbon and hydrogen in the crude petroleum include sulfur, oxygen, and nitrogen.

Since crude oil is composed of hydrocarbons of different physical properties, it can be separated by physical means into its various constituents. In practice, primary separation is usually accomplished by distillation, with collected fractions consisting of hydrocarbons of specified boiling ranges. The fractions usually include refinery gas, gasoline, kerosine, light fuel oil, diesel oils, gas oil, lube distillate, and heavy bottoms, the amount of each being determined by the type and composition of the crude oil. These are called straight run prod-

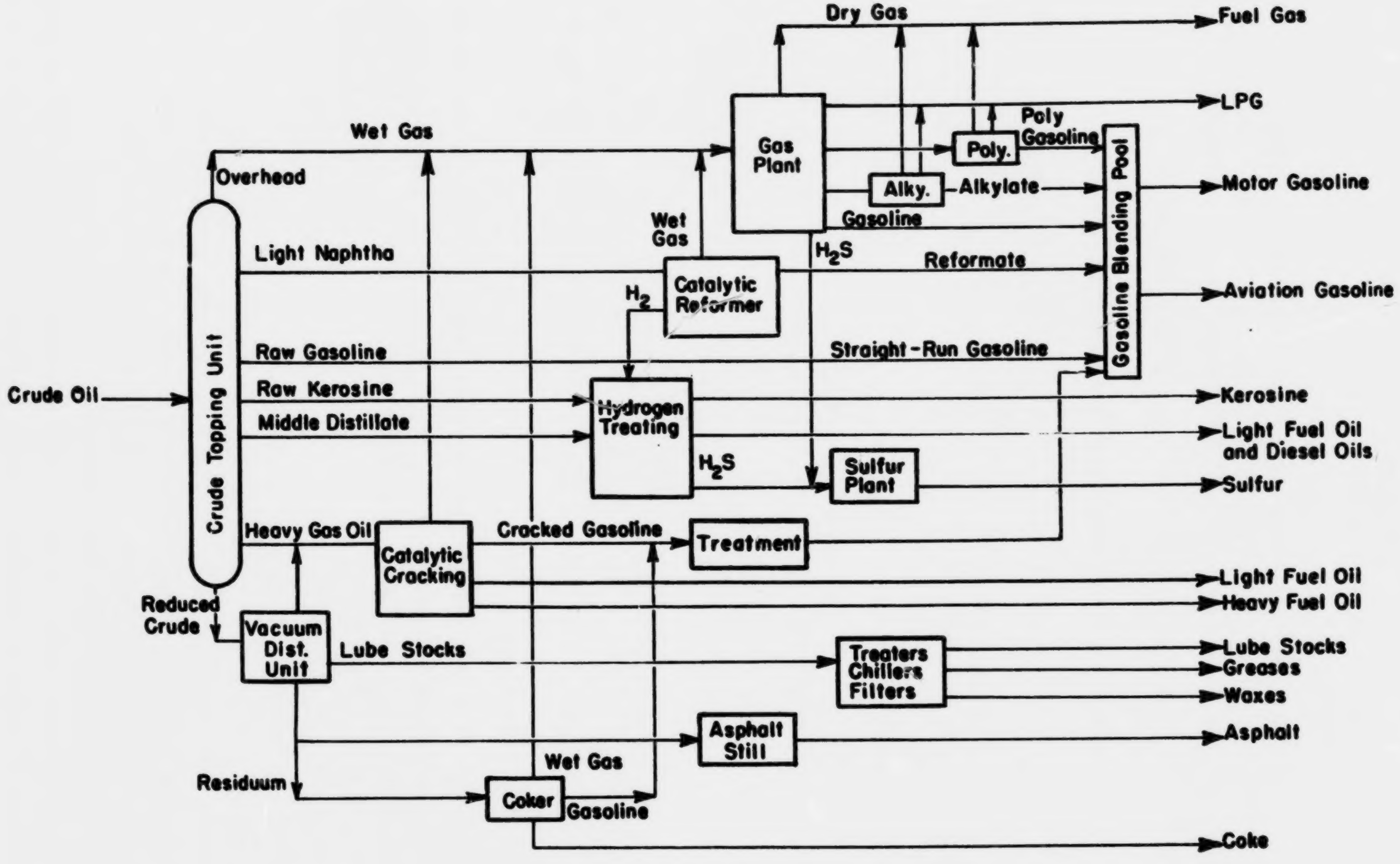
Crude Oil
Crude Topping Unit
Overhead
Wet Gas
Light Naphtha
Raw Gasoline
Raw Kerosine
Middle Distillate
Heavy Gas Oil
Reduced Crude
Vacuum Dist. Unit
Lube Stocks
Residuum
Catalytic Cracking
Cracked Gasoline
Treatment
Coker
Wet Gas
Gasoline
Asphalt Still
Treaters Chillers Filters
Hydrogen Treating
H_2S
Sulfur Plant
H_2
Catalytic Reformer
Wet Gas
Gas Plant
Dry Gas
H_2S
Gasoline
Alky.
Alkylate
Poly.
Poly Gasoline
Reformate
Straight-Run Gasoline
Gasoline Blending Pool
Fuel Gas
LPG
Motor Gasoline
Aviation Gasoline
Kerosine
Light Fuel Oil and Diesel Oils
Sulfur
Light Fuel Oil
Heavy Fuel Oil
Lube Stocks
Greases
Waxes
Asphalt
Coke

FIGURE 3. *Processing plan for complete modern refinery*

ucts. Some are treated to remove impurities and used as base stocks or sold as finished products; the remainder are used as feedstock for other refinery units.

Primary separation is accomplished by simple distillation in crude topping or skimming units. Crude is heated in pipe stills and passed to fractionating towers or columns for vaporization and separation. Heavy fractions of the crude which do not vaporize in the topping operation are separated by steam or vacuum distillation. These processes accomplish vaporization of the high-boiling fractions at relatively low temperatures by maintaining a vacuum above the hot oil in the tower or by introducing into the tower an inert gas, usually steam or recycled vapor, to lower the partial pressure in the vapor. Destructive distillation and coking are severe forms of reduction employed to convert heavy residuum to coke and more valuable volatile products.

Combinations of all of these methods and occasionally solvent extraction and adsorption techniques are used to separate crude oil in most refineries, the combination being determined by the boiling range of the stock, the stability of the stock with respect to heat, and product specifications. Figure 4 shows a typical crude oil distillation unit.

Conversion

The relative amounts of various products obtained by a simple separation of crude oil usually do not conform to the existing demand for these products. For example, the yield of gasoline from the separation of most crude oils is about 25 percent of the volume of crude processed. However, the crude must be made to yield almost 50 percent gasoline to supply the demand for gasoline without producing excess quantities of other crude oil constituents such as kerosine, fuel oil, and heavy residuum. Also, much of the gasoline must be of better quality than occurs naturally in the crude oil.

To obtain a more desirable product distribution and quality, heavy hydrocarbon molecules are cracked or split to form low-boiling hydrocarbons in the gasoline range, and light gaseous hydrocarbons are united in polymerization or alkylation units to form gasoline blending stock. The processes of reforming and isomerization rearrange the molecular structure of gasoline to produce a higher octane fuel with better performance characteristics.

Cracking

In the cracking operation, large molecules are decomposed by heat and pressure (sometimes using catalysts) into smaller, lower-boiling molecules. At the same time, some of the molecules combine (polymerize) to form larger molecules. The products of cracking are gaseous hydrocarbons, gasoline, gas oil, fuel oil, and coke.

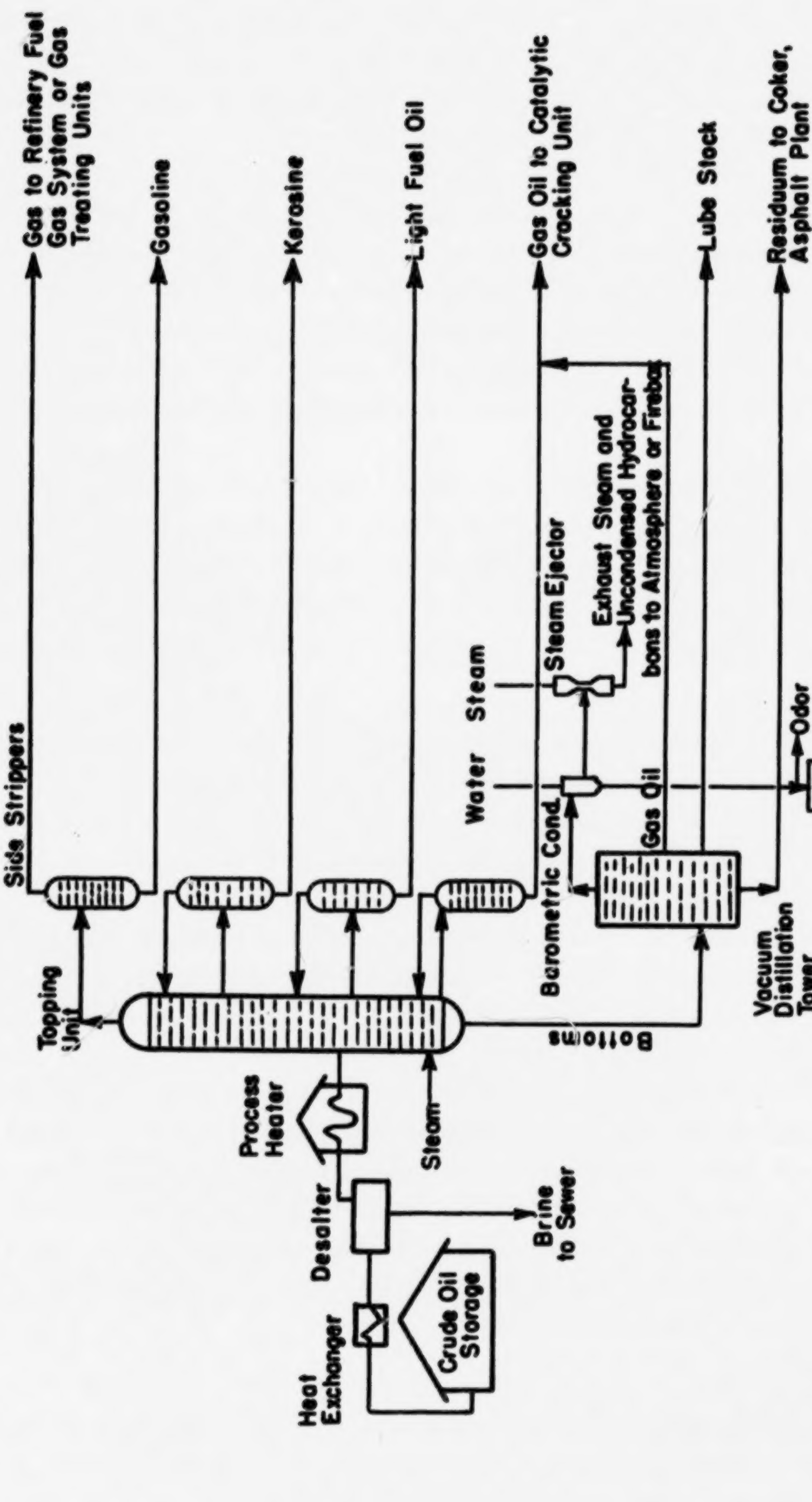
Heat Exchanger
Crude Oil Storage
Desalter
Brine to Sewer
Process Heater
Steam
Topping Unit
Bottoms
Side Strippers
Barometric Cond.
Vacuum Distillation Tower
Water
Steam
Steam Ejector
Exhaust Steam and Uncondensed Hydrocarbons to Atmosphere or Firebox
Gas Oil
Odor
Condenser Sump
to Separator
Gas to Refinery Fuel Gas System or Gas Treating Units
Gasoline
Kerosine
Light Fuel Oil
Gas Oil to Catalytic Cracking Unit
Lube Stock
Residuum to Coker, Asphalt Plant

FIGURE 4. *Typical crude unit employing topping and vacuum distillation*

Thermal Cracking

Thermal cracking is giving way to catalytic cracking. However, thermal cracking still constitutes about one-third of the total cracking capacity in the United States, equivalent to about 20 percent of total refinery crude capacity.

In thermal cracking units, the charge stock, usually a topped crude or other heavy residual product, is heated to about 1,000° F. at high pressures to produce gaseous hydrocarbons, gasoline, gas oil, and residual fuel oil. A small amount of coke is deposited in the coils of the heater and reactor, and the units must be shut down periodically for cleaning.

Other forms of thermal cracking may include coking, a severe cracking operation; visbreaking, a mild cracking to reduce the viscosity of the feedstock, usually fuel oil; and combination units which combine crude oil distillation and some form of cracking.

Catalytic Cracking

Catalytic cracking is the backbone of the modern refinery. The capacity of these units amounts to about 4 million barrels per day, equivalent to about 40 percent of total refinery crude capacity. Cracking over a catalyst, usually an alumina-silicate, is accomplished at slightly greater than atmospheric pressures and about 900° F. It gives a higher gasoline yield and better quality gasoline than thermal cracking. The charge stock is usually gas oil, a distillate intermediate between kerosine and fuel oil. Catalytic cracking yields a "synthetic crude" which is separated into gaseous hydrocarbons, gasoline, gas oil, and fuel oil.

During the cracking process, which is usually continuous, coke deposits on the catalyst and is burned off in separate regenerating vessels.

Catalytic cracking units may be classified according to the method used for catalyst transfer. There are four main methods: (1) fixed-bed, utilizing a number of reaction-regeneration chambers in a batch-type operation, (2) moving-bed, (3) fluidized bed, and (4) a once-through catalyst system which does not attempt catalyst regeneration. Fixed-bed and once-through systems are no longer used to any great extent. The moving-bed system, typified by the Thermofor Catalytic Cracking Units (T.C.C.), and the Houdriflow Units, and the fluidized bed or Fluid Catalytic Cracking Units (F.C.C.) are now almost universally used in refinery operations.

A typical moving-bed "cat" cracker is shown in figure 5. The catalyst, in the form of beads or pellets, passes through the reactor, then through a regeneration zone where coke deposited on the catalyst is burned off in a continuous process. The regenerated catalyst is lifted by air, or in the older units by bucket elevators, to catalyst storage bins atop the reactor vessel.

In fluidized systems, figure 6, finely powdered catalyst is lifted into the reactor by the incoming oil charge, which vaporizes upon contact with the hot catalyst. The catalyst which does not settle out in the reactor is removed from the cracked product stream by a system of cyclonic separators located in the reactor vessel. Catalyst is drawn off at a controlled rate, purged with steam, and lifted into the regenerator by a stream of air where the coke is removed by burning. The regenerator flue gases containing entrained catalyst pass through a series of cyclonic separators in the regeneration vessel, often followed by an electrostatic precipitator, before discharge to the atmosphere.

Catalytic Reforming

In the past 7 years there has been a tenfold increase in the use of catalytic reforming by oil refineries, and the present capacity is nearly 2 million barrels per day. Unlike catalytic cracking, catalytic reforming does not increase the gasoline yield from a barrel of crude oil; it uses gasoline as a feedstock and by molecular rearrangement, usually including hydrogen removal, produces a gasoline of higher quality and octane number, along with large quantities of hydrogen.

Some fixed-bed installations have facilities for the regeneration of the catalyst in place with the resulting discharge of combustion products. Since coke deposition is not severe in reforming operations, catalyst regeneration in place is not always used. In this case, the

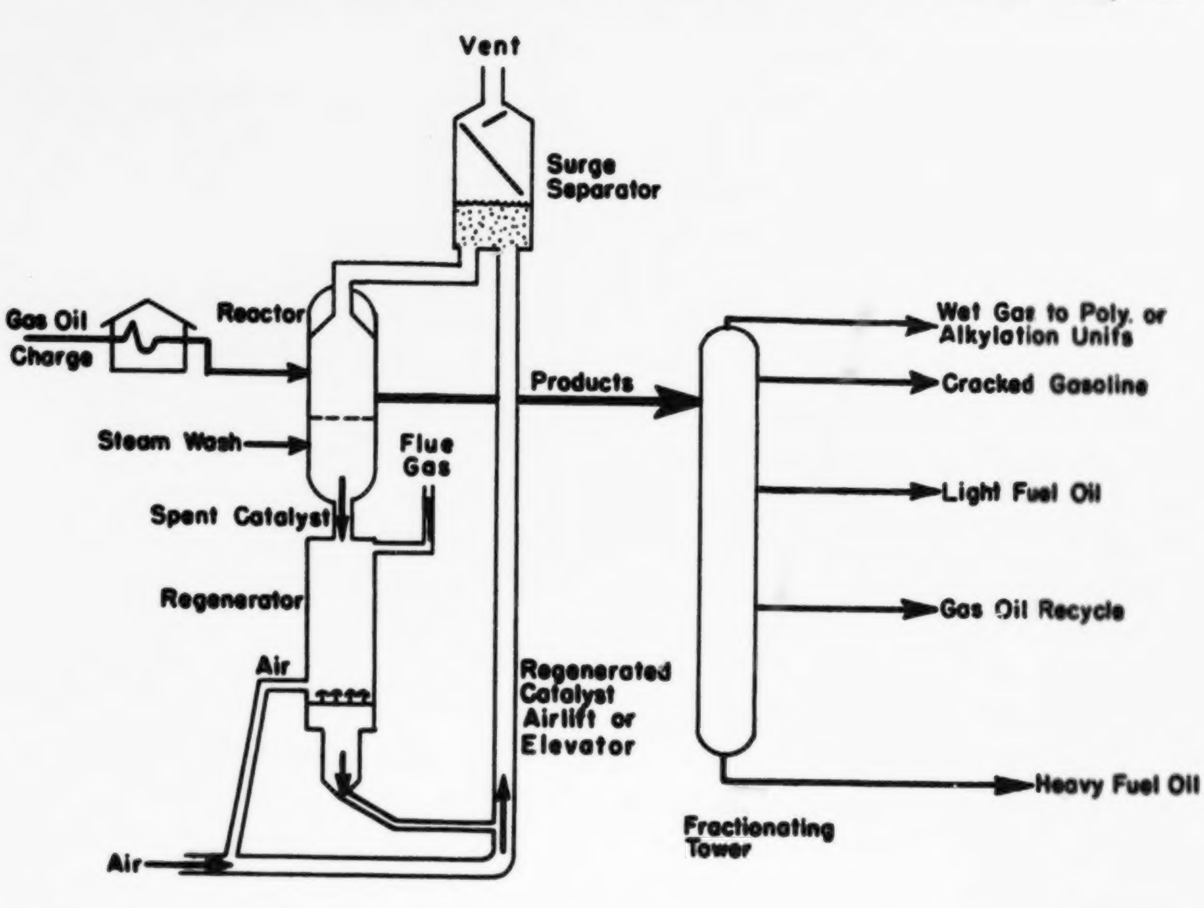
Vent
Surge Separator
Gas Oil Charge
Reactor
Steam Wash
Flue Gas
Spent Catalyst
Regenerator
Air
Regenerated Catalyst Airlift or Elevator
Air
Products
Wet Gas to Poly. or Alkylation Units
Cracked Gasoline
Light Fuel Oil
Gas Oil Recycle
Heavy Fuel Oil
Fractionating Tower

FIGURE 5. *Typical moving-bed catalytic cracking unit, similar to Thermofor Catalytic Cracking (T.C.C.) and Houdry processes*

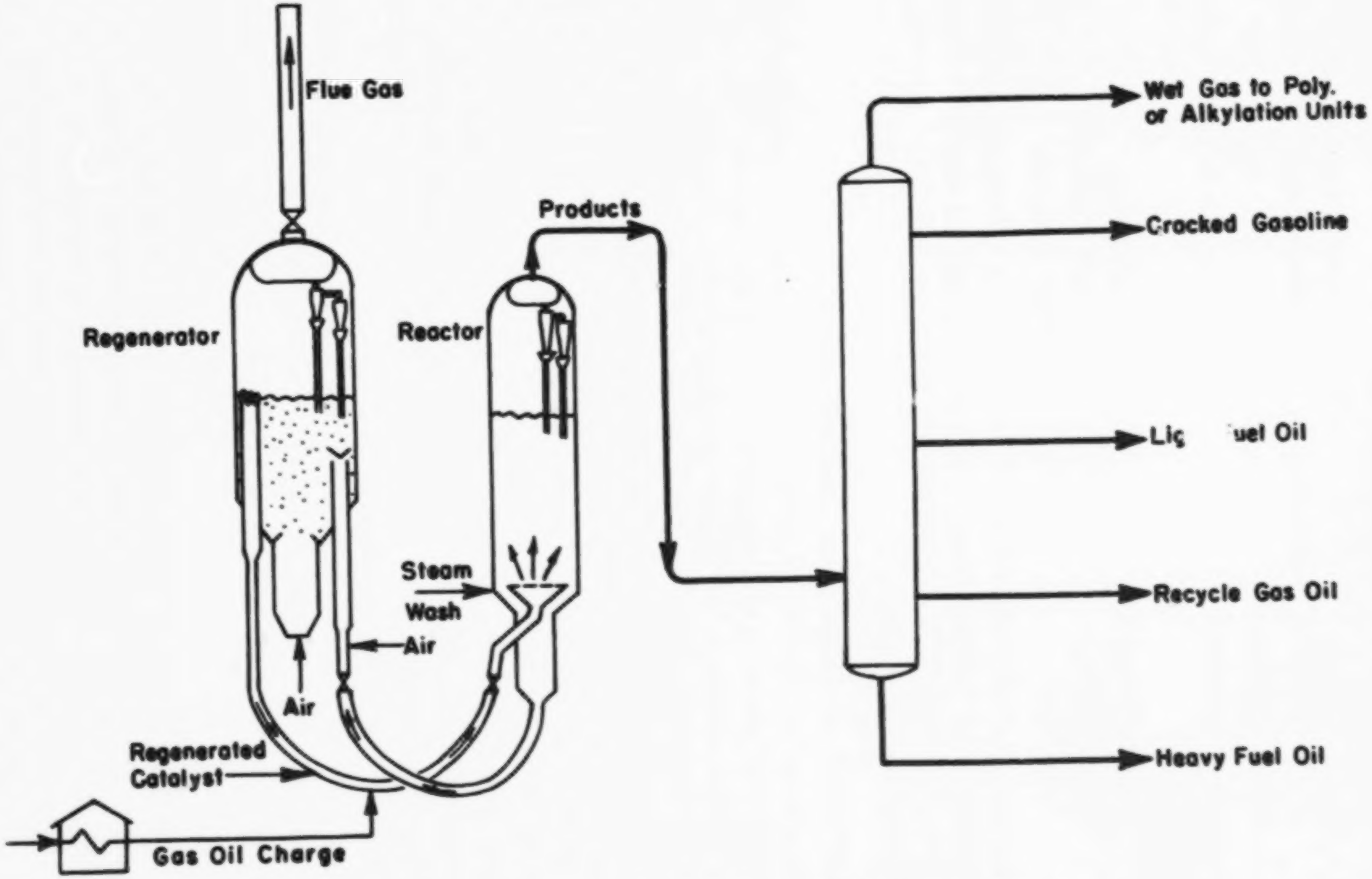
Flue Gas
Regenerator
Reactor
Products
Steam
Wash
Air
Air
Regenerated Catalyst
Gas Oil Charge
Wet Gas to Poly. or Alkylation Units
Cracked Gasoline
Light Fuel Oil
Recycle Gas Oil
Heavy Fuel Oil

FIGURE 6. *Fluidized bed catalytic cracking unit.* (*F.C.C.*)

catalyst is physically removed and replaced periodically. The following lists include most commercial fixed-bed catalytic reforming processes (3).

Fixed-bed processes which require regeneration of catalyst in place:

Cycloversion
Fixed-Bed Hydroforming
Ultraforming
Sinclair—Baker Kellogg
Powerforming

Fixed-bed processes in which the catalyst is infrequently regenerated:

Platforming
Rexforming
Iso-Plus
Catforming
Houdriforming
Sovaforming

Also commercially available are two fluidized processes, Fluid Hydroforming and Orthoforming, and one moving-bed type, Thermofor Catalytic. These three types use continuous catalyst regeneration similar to cracking units.

Polymerization, Alkylation, Isomerization

Polymerization and alkylation are processes used to produce gasoline from the gaseous hydrocarbons formed during cracking operations. Polymerization joins two or more olefins (noncyclic unsaturated hydrocarbons with $C=C$ double bonds), and alkylation unites an olefin and an iso-paraffin (noncyclic branched-chain hydrocarbon saturated with hydrogen). Isomerization is the process for altering the arrangement of atoms in a molecule without adding or removing anything from the original material, usually used in the oil industry to form branched-chain hydrocarbons. A number of catalysts such as phosphoric acid, sulfuric acid, platinum, aluminum chloride, and hydrofluoric acid are used to promote the combination or rearrangement of these light hydrocarbons.

These three processes, including regeneration of any necessary catalysts, form essentially closed systems and they have no unique, major source of atmospheric emissions.

Treating

As noted earlier, crude oils may contain small amounts of many impurities. Sulfur is a major undesirable constituent in petroleum from a refining standpoint; also, some attention is being given to nitrogen which may adversely affect the catalysts used in some processes.

Sulfur in crude oil is usually found in combination with hydrogen or hydrocarbons as hydrogen sulfide (H_2S), mercaptans ($R{-}SH$), sulfides ($R{-}S{-}R$), polysulfides ($R{-}S_x{-}R$) and thiophenes, ring compounds with sulfur as a member of the ring structure. During the refining process, part of the original sulfur compounds is often converted to H_2S and to lower molecular weight mercaptans.

Sulfur removal from both product and intermediate feedstocks is becoming more universal in oil refineries for a number of reasons, including improved product quality, sensitivity of certain catalysts to sulfur poisoning, and the use of crude oils relatively high in sulfur content due to the depletion of low sulfur crudes. At the present time about 40 percent of the crude oil produced in the United States contains over 0.5 percent sulfur, and about 10 percent of the crude contains over 2 percent sulfur. The cost of removing this sulfur may amount to 10 to 15 percent of total refinery operating expenses (6). Although treatment varies widely, some degree of removal is necessary because of the effect sulfur has on refinery processes and product quality. Sulfur compounds are frequently odorous and may cause corrosion, reduce octane number and lead susceptibility, decrease yields from cracking operations, poison certain catalysts, and adversely affect product qualities such as stability and burning characteristics.

Petroleum products and feedstocks are treated by many methods, utilizing both physical separations and chemical reactions.

Hydrogen Treating

Catalytic hydrogen treating is relatively new, but it is becoming a widely used method of removing impurities from petroleum products. It involves a mild selective hydrogenation which converts organic compounds of sulfur, nitrogen, and oxygen into hydrocarbons and removable hydrogen sulfide, ammonia, and water. In addition the process converts diolefins, gum-forming hydrocarbons, into stable compounds, while minimizing saturation of desirable aromatics. Hydrogen treating requires large quantities of relatively pure hydrogen, most economically supplied by catalytic reforming units, and the two processes—catalytic reforming and hydrogen treating—are often found together. Some new installations combine hydrogen treating and catalytic reforming into a two-stage integrated unit.

Nearly all hydrogenation units are the fixed-bed type. Catalyst replacement or regeneration cycles vary from a few days to greater than a year, depending on operating conditions and the product being treated; high temperatures and heavy feedstocks accelerate coke deposition on the catalyst and force frequent regeneration. The catalyst is regenerated in the usual manner by controlled combustion of the deposited coke. Hydrogen sulfide is removed from the hydrogen stream in an extraction system and converted to elemental sulfur or sulfuric acid; or when the quantity is too small to justify recovery, is burned to SO_2 in a flare or boiler firebox.

Chemical Treating

A number of chemical methods are used throughout the refinery to treat hydrocarbon streams. Equipment used for most chemical treating units includes a mixing chamber, a separation vessel, a water wash system, and, in some processes, a regeneration unit to reactivate or recover spent chemicals. Chemical treatments can conveniently be classified into four groups: (1) acid treatment, (2) sweetening, (3) solvent extraction, and (4) additives.

Acid treatment involves contacting the hydrocarbons with concentrated sulfuric acid which partially removes sulfur and nitrogen compounds, precipitates asphaltic or gum-like materials, and improves color and odor. Where this type of process is still used, spent acid sludges are usually converted to ammonium sulfate or sulfuric acid.

Sweetening processes oxidize mercaptans to disulfides, without actual removal of sulfur. The most common sweetening processes are the doctor (sodium plumbite), lead sulfide, hypochlorite, and copper chloride processes. In some sweetening processes, air and steam are used for agitation in mixing tanks and also to reactivate chemical solutions.

Treatment by solvent extraction involves the use of a solvent with an affinity for the undesirable compounds, and which can be separated easily from the product stream. Sulfur compounds, particularly mercaptans, are extracted using a strong caustic, sometimes fortified with solubility promoters such as alcohol, organic acids, or alkyl phenols. Commercial processes of this type include the Tannin-Solutizer, Mercapsol, Unisol, and Dualayer processes. The solvents are usually regenerated by heat, steam stripping, or air blowing.

Hydrogen sulfide is removed from both gaseous and liquid hydrocarbon streams by solvent extraction in a number of commercial processes including the Girbotol, Phenolate, Alkazid, Ferrox, Phosphate, and Glycol-Amine processes.

Additives or inhibitors are primarily materials added in small amounts to oxidize mercaptans to disulfides and retard gum formation.

Treatment by Physical Means

Physical methods, including electrical coalescence, filtration, absorption, and air blowing, are often used in refineries to treat hydrocarbon streams or remove undesirable components as intermediate steps in the processing scheme. Applications include desalting crude oil, wax removal, decolorizing lube oils, and brightening diesel oil (removal of turbidity due to moisture).

Blending

The oil industry produces almost 2,500 finished petroleum products. These include over 10 types of liquefied gases, about 40 different gasolines, nearly 300 types of greases, and over 1,000 different lubricating oils. These products each conform to separate specifications, often including standards for vapor pressure, specific gravity, sulfur content, viscosity, octane number, initial boiling point, pour point, etc. The many products are made, or fabricated, by blending relatively few refinery base stocks in varying proportions until the desired products are obtained.

Atmospheric Emissions From Oil Refineries

Refineries vary greatly in both the quantity and type of emissions. The most important factors affecting refinery emissions are crude oil capacity, air pollution control measures in effect, general level of maintenance and good housekeeping in the refinery, and the processing scheme employed. The emissions which may contribute to air pollution are sulfur oxides, nitrogen oxides, hydrocarbons, carbon monoxide, and malodorous materials. Other emissions of lesser importance include particulates, aldehydes, ammonia, and organic acids. Table 2 indicates potential sources of the various contaminants from refineries and emphasizes the variety of equipment and operations which must be considered in a complete survey of refinery emissions. An attempt to categorize these potential sources into the four major refinery operations of separation, conversion, treating, and blending developed in the preceding section on refinery technology is difficult because many of the potential sources such as pipeline valves are found throughout the refinery, while others such as waste gas flares cannot be assigned to any one refinery operation. Rather, for an air pollution survey an oil refinery should be considered an integrated system of pumps, valves, cooling towers, process heaters, and other equipment and operations listed in table 2. These are the primary sources of possible emissions, and an estimate of emissions is best accomplished by summing the contribution of each of these potential sources.

TABLE 2. *Potential sources of specific emissions from oil refineries*

Emission	Potential sources
Oxides of sulfur	Boilers, process heaters, catalytic cracking unit regenerators, treating units, H_2S flares, decoking operations.
Hydrocarbons	Loading facilities, turnarounds, sampling, storage tanks, waste water separators, blow-down systems, catalyst regenerators, pumps, valves, blind changing, cooling towers, vacuum jets, barometric condensers, air-blowing, high pressure equipment handling volatile hydrocarbons, process heaters, boilers, compressor engines.
Oxides of nitrogen	Process heaters, boilers, compressor engines, catalyst regenerators, flares.
Particulate matter	Catalyst regenerators, boilers, process heaters, decoking operations, incinerators.
Aldehydes	Catalyst regenerators.
Ammonia	Catalyst regenerators.
Odors	Treating units (air-blowing, steam-blowing), drains, tank vents, barometric condenser sumps, waste water separators.
Carbon monoxide	Catalyst regeneration, decoking, compressor engines, incinerators.

While it is not practicable to make a survey of refinery emissions based on the refinery divisions of separation, conversion, treating, and blending, it is helpful to consider in a general way the major or unique sources for each of these major operations, and to indicate the possible emissions in a qualitative manner.

Of special interest in the separation of crude oil into petroleum products is the barometric condenser sometimes used to maintain a vacuum on the vacuum distillation tower. Noncondensables, including light hydrocarbons, pass through the condenser and may be discharged to the atmosphere. This can be a major source of hydrocarbon emissions, depending on the size of the unit, the type of feedstock, and the temperature of the cooling water. In addition, the condenser sump may be a source of odor emissions.

Cracking operations may be a significant source of atmospheric emissions because of the necessity for removing the coke which forms during cracking operations. The coke deposits on the catalyst itself or in the reactor tubes during thermal cracking operations and may include sulfur and other impurities present in the feedstock. It is usually removed by a controlled combustion process with resulting discharge of the combustion gases including catalyst fines, unburned hydrocarbons, sulfur oxides, carbon monoxide, ammonia, and nitrogen oxides. A persistent plume will often accompany the discharge from catalytic cracking unit regenerators. In addition to combustion gases, catalyst fines may be discharged by vents on the catalyst handling systems on both T.C.C. and F.C.C. units.

The conversion processes of alkylation, polymerization, and isomerization, although having no unique source of potential emissions, deserve special mention. The highly volatile nature of the hydrocarbons handled and the high process pressures required make valve stems and pump shafts difficult to seal, and a greater emission rate from these two sources can generally be expected in these process areas than is normal throughout the refinery. It is generally true that processes or refineries handling L.P.G., gasoline, or other highly volatile products will have a higher hydrocarbon emission rate than similar processes or refineries limited to production of lubricants, asphalts, fuel oils, or other materials with low vapor pressures.

Emissions from treating operations may vary widely and depend particularly on the methods used for handling spent acid and acid sludges, and on the method employed for recovery or disposal of the hydrogen sulfide. These operations are potential sources of sulfur oxides, hydrocarbons, and visible plumes. Other potential sources of SO_2, hydrocarbons, and particulate matter in the treating area include catalyst regeneration, air agitation in mixing tanks, and other air blowing operations. Trace quantities of malodorous substances such as H_2S and mercaptans may escape from numerous sources throughout the treating area including settling tank vents, surge tanks, water treatment units, waste water drains, valves, and pump seals.

Pipeline blind changing is a potential source of hydrocarbon emission generally found concentrated in the refinery product blending area. Blinds are circular metal plates inserted into the pipeline at flanged connections to insure product separation and minimize the possibility of accidental product mixing. During blind changing operations some hydrocarbons probably escape.

The Joint Project (2) evaluated emissions from petroleum refineries in Los Angeles County by an extensive study of most of the primary sources of emissions listed in table 2, usually with a field testing program.

A knowledge of these potential sources, their distribution in the refinery, the mode of escape, and the type and magnitude of emissions for refineries in Los Angeles County can aid in making air pollution surveys in other areas. However, care must be taken in the use of Joint Project loss data for estimating losses from other refineries. Processing schemes may not be the same and may influence the type and amount of emissions. The following list summarizes the process capacities for refineries in Los Angeles County during the Joint Project investigations:

Distillation units—685,000 barrels charged per calendar day.
Vacuum distillation—310,000 barrels charged per calendar day.
Thermal operations—280,000 barrels charged per calendar day.
Catalytic cracking, total feed—290,000 barrels charged per calendar day.
  Percent recycle—25 percent.
Catalytic reforming—58,000 barrels charged per calendar day.
Hydrogen treating—41,000 barrels charged per calendar day.
Alkylation—33,000 barrels produced per calendar day.
Polymerization—4,000 barrels produced per calendar day.
Lube—230 barrels produced per calendar day.
Asphalt—25,000 barrels produced per calendar day.
Coke—1,000 tons produced per calendar day.

It should be borne in mind that, due to the unique topographical and climatic conditions in the area, emissions from refineries in Los Angeles County are controlled to a high degree. The Los Angeles County Air Pollution Control District enforces a number of rules and regulations, some of which apply specifically to the oil industry in that area. These rules specify types of storage tanks which may be used, require controls on waste water separators and gasoline loading operations, and limit the emission of dusts, smoke, and SO_2.

In complying with these regulations and inaugurating voluntary control and employee educational programs, oil refineries in Los

Angeles County in the past 10 years have reduced sulfur emissions by 600 tons daily and controlled several hundred tons of hydrocarbons per day, at a cost of about $33 million. Because of the emphasis placed on air pollution control in Los Angeles, the Joint Project (2) emission figures approach the lowest values currently obtainable.

Sources of Emissions From Oil Refineries in the Los Angeles Area

This section of the manual enumerates sources of emissions from oil refineries in the Los Angeles area, summarizes the results of the Joint Project studies, gives average data on emissions, and describes control measures applied by these refineries.

Storage Tanks

Storage tanks are an important source of hydrocarbon emissions in petroleum refineries. Hydrocarbon vapors may be released through a number of mechanisms, including tank breathing caused by temperature changes, displacement during filling operations, and a small amount of direct evaporation from tanks equipped with floating roofs.

The Joint Project canvassed all refineries in Los Angeles concerning hydrocarbon storage. The information requested for each tank included capacity, dimensions, type of roof, controls, construction and maintenance, product stored, vapor pressure of product, average throughput, and other data in sufficient detail to allow calculation of vapor losses. Losses were calculated using equations and nomographs presented at the 32d Annual Meeting of the American Petroleum Institute (7). This method of calculation, along with a calculation sheet, is shown in appendix I. This method of calculation is now in process of modification. Reference should be made to API Bulletins 2512, 2513, and others planned on this subject for up-to-date information on the magnitude, causes, and control of evaporation losses.

In 1956, refineries in Los Angeles County had 135 crude oil storage tanks and 704 tanks for distillate products, with capacities of 7.4 and 20.8 million barrels respectively. The calculated emissions from crude oil storage tanks amounted to 15 tons per day and from distillate tanks were 27 tons per day. It was assumed that no emissions occurred from pressure storage of liquefied petroleum gases (L.P.G.). These emissions are not typical for an area processing 700,000 barrels of crude daily.

All refineries have some facilities to reduce hydrocarbon emissions to the economic level. For the reasons previously mentioned, however, refineries in the Los Angeles area are required to exercise an even greater degree of control than has been found necessary in other areas. For example, a control rule (rule 56) has been established which applies to all tanks of greater than 40,000-gallon capacity which store petroleum distillate products having vapor pressures greater than 1.5 p.s.i.a. under actual storage conditions. Under this rule floating roof tanks are permissible for materials with vapor pressures not exceeding 11 p.s.i.a. at storage temperature, and vapor recovery systems are required for storage tanks handling more volatile materials. Although crude oil storage is not covered by rule 56, over two-thirds of crude storage capacity in Los Angeles is in tanks with some form of vapor control.

Table 3 presents average loss figures for storage in fixed roof and floating roof tanks in the Los Angeles area. These averages are not a direct measure of the relative effectiveness of various types of tanks. (Refer to the publications of the API Evaporation Loss Committee, Bulletins 2512, 2513.) Tanks connected to vapor recovery systems were assumed to have no loss.

TABLE 3. *Average hydrocarbon emission factors for refinery storage tanks in the Los Angeles area*

Material stored	Emission factor (pounds of hydrocarbon per day per 1,000 barrel storage capacity)		Material stored	Emission factor (pounds of hydrocarbon per day per 1,000 barrel storage capacity)	
	Fixed roof	Floating roof		Fixed roof	Floating roof
Crude oil:			Petroleum distillate:		
Vapor pressure >1.5 p.s.i.a.	9.1	4.8	Vapor pressure >1.5 p.s.i.a.	*47	4.8
Vapor pressure <1.5 p.s.i.a.	4.5	1.8	Vapor pressure <1.5 p.s.i.a.	1.6	1.7

*All tanks in this group were of less than 1,000 barrels capacity. Larger tanks would have somewhat lower emission factors.

Catalyst Regeneration Units

During catalytic cracking, reforming, and hydrogenation, coke formed on the surface of the catalyst is burned off in regenerating vessels by controlled combustion. The flue gases from the catalyst regenerator may contain fine catalyst dust, and the products of combustion of the coke may include some of the impurities contained in the charging stock. Cracking unit regenerators are usually large and operate continuously and are potential sources of dust, carbon monoxide, hydrocarbon (nearly all methane), and sulfur oxide emissions. Reforming and hydrogen treating units usually regenerate catalysts intermittently and are a less important source of emissions.

Table 4 summarizes the results of the Joint Project data on emissions from catalytic cracking unit regenerators. It should be noted that because of higher catalyst circulation rates, Fluid Units (F.C.C.) have significantly higher average emission rates than Thermofor (T.C.C.) Units, based on unit capacity. Also, the values for all emissions vary greatly, even between the same types of units. Therefore, the use of average values may introduce large inaccuracies.

One Thermofor Catalytic Reformer Unit (T.C.R.) was tested and had emissions similar to the T.C.C. units, except for sulfur emissions, which were very low.

Dust emissions in Los Angeles County are limited to 40 pounds per hour from any one unit, processing in excess of 60,000 pounds per hour. To meet this regulation, all T.C.C. units in refineries in Los Angeles County are equipped with high-efficiency cyclonic separators; F.C.C. units are controlled by more elaborate dust removal equipment, including cyclones and electrostatic precipitators.

Pipeline Valves and Flanges

Under the influence of heat, pressure, vibration, friction, and corrosion, valves and flanged connections may develop leaks. These leaks may be liquid, vapor, or both, depending on the product carried and on temperature.

Tests made on almost 10,000 valves indicated a total emission from all valves of 10 tons per day. Average emissions were 0.5 pound of hydrocarbons per day from valves handling light materials (vapor pressure greater than 15 p.s.i.a. at 60° F.), and average vapor emissions of 0.05 pound per day from valves handling heavier, liquid products. Emissions from this source averaged 28 pounds per day per 1,000 barrels of crude throughput.

TABLE 4. *Emissions from catalytic cracking unit regenerator stacks, Los Angeles area refineries*

	Type of catalytic cracking unit		Total all units
	Fluid	Thermofor	
Number of units	6	9	15
Fresh feed rate, barrels per day	156,000	69,000	225,000
Recycle feed rate, barrels per day	35,000	38,000	73,000
Catalyst circulation rate, tons per hour	14,000	1,400	15,400
Stack discharge rate, SCFM, 60° F. and 1 atm. (dry basis)	484,000	134,000	618,000
Emissions:			
Hydrocarbons, p.p.m. range	98-1213	87-1655	87-1655
Tons per day	17	3	20
Sulfur dioxide, p.p.m. range	308-2190	65-141	65-2190
Tons per day	41	2	43
Sulfur trioxide, tons per day	2.3	0.4	2.7
Ammonia, as NH_3, p.p.m. range	67-675	29-103	29-675
Tons per day	4.2	0.2	4.4
Aldehydes, as HCHO, p.p.m. range	3-130	9-177	3-177
Tons per day	1.5	0.4	1.9
Oxides of nitrogen, as NO_2, p.p.m. range	8-394	7-62	7-394
Tons per day	4.9	0.3	5.2
Cyanides, as HCN, p.p.m. range	0.19-0.94	0.07-0.7	0.07-0.94
Tons per day	0.01	0.002	0.012
Total particulate matter, tons per day	4.8	0.6	5.4
Carbon monoxide, volume percent	0-7.8	0-4.1	0-7.8
Tons per day	1,070	130	1,200

Tests made on pipeline flanges indicated negligible emissions from this source.

Pressure Relief Valves

The pressure relief valves commonly used by oil refineries are spring loaded and fitted with a discharge pipe called a "horn" (fig. 7). Horns are often manifolded to a common header or a blowdown system; occasionally they are fitted with steam purge lines for fire control or to aid the dispersion of gases.

Corrosion may cause pressure relief valves to reseat improperly after blowoff. Since routine maintenance and observation are sometimes difficult because of inaccessibility, relief valve installations can leak substantially before repair. The Joint Project study considered only valve leakage; emissions due to pressure relief valve blowoffs were not considered.

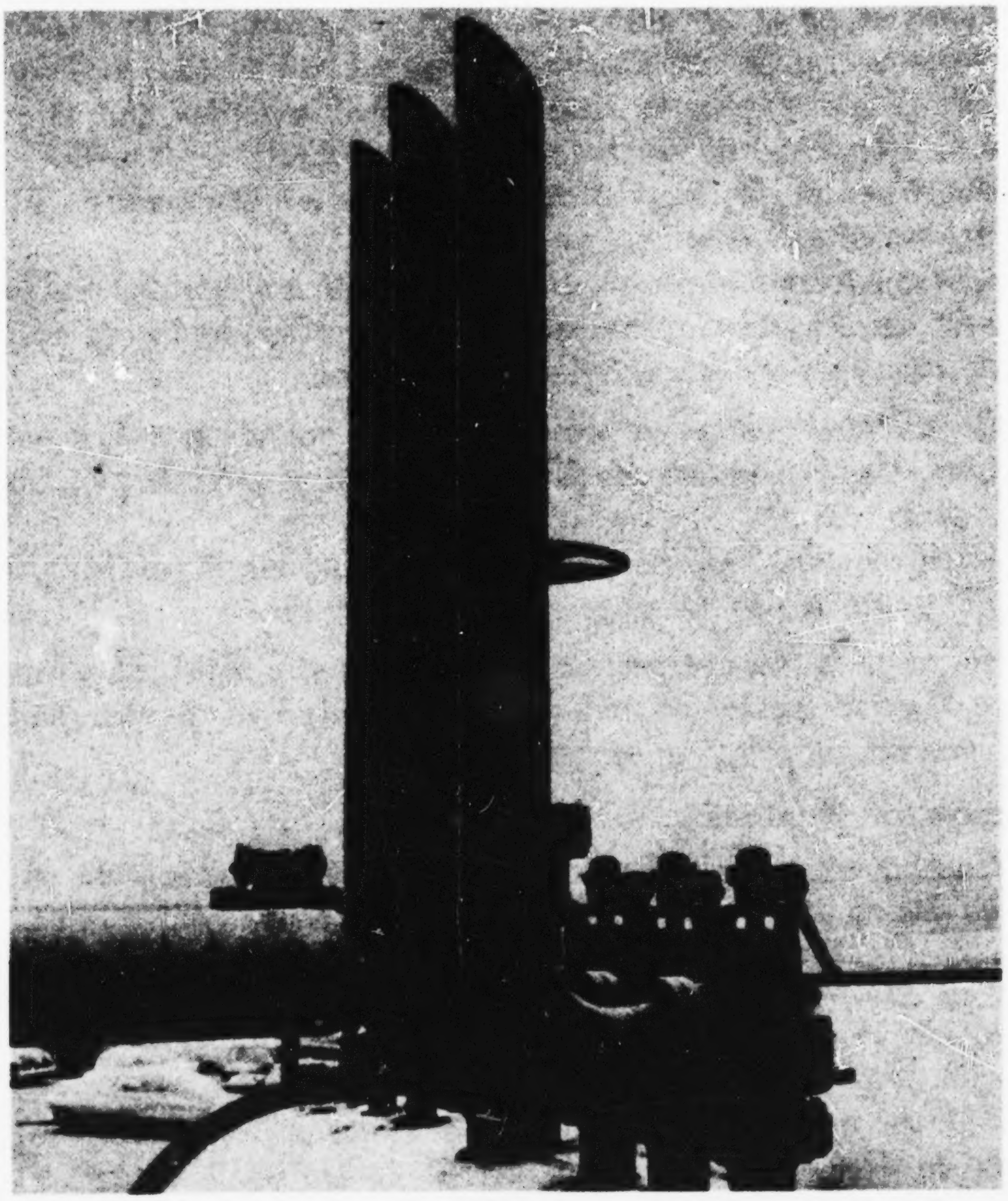

FIGURE 7. *Typical pressure relief installation showing three single-type relief valves*

NOT REPRODUCIBLE

Over 400 pressure relief valves were tested. These had average emissions of 2.9 pounds per day for valves on operational vessels, and 0.6 pound per day for valves on pressure storage tanks. The total emission was 3,500 pounds per day from almost 1,500 valves. An additional 1,800 relief valves were manifolded to vapor recovery or blowdown systems and had no emission to the atmosphere. The leakage from valves on liquid lines was negligible.

Pumps and Compressors

Pumps and compressors can leak product at the contact between the moving shaft and stationary casing. Packing and mechanical seals are almost universally used in oil refineries to retard leakage through this junction. Packing or packed seals retard leakage by forcing asbestos or other fibers around the shaft, and can be used to seal both rotary and reciprocating shaft motions. Mechanical seals have two plates set perpendicular to the shaft, one stationary and connected to the pump casing, and a second connected to the shaft and rotating with it. These plates, or rings, are forced together and effect the closure. In normal service both packed and mechanical seals can leak product when shafts become scarred or move eccentrically, or when the packing or seal faces become defective.

Emissions from pump seals in the Los Angeles area refineries totaled about 6 tons of hydrocarbons per day, with average hydrocarbon losses for various types of seals and pumps as follows:

Centrifugal pumps—packed seals—4.8 pounds per day per seal
Centrifugal pumps—mechanical seals—3.2 pounds per day per seal
Reciprocating pumps—packed seals—5.4 pounds per day per seal
All pump seals—4.2 pounds per day per seal

Tests on over 300 compressor seals indicated a total loss from this source of 1.5 tons per day, and an average daily hydrocarbon emission of 8.5 pounds per compressor seal.

Compressor Engines

Gas compressors are often driven by internal combustion engines, usually fueled by natural or refinery gas. Although these engines are normally operated at steady load conditions and have good efficiency, as in all engines of this type, some of the fuel passes through the engine and out the exhaust unburned. In addition, as a result of nitrogen fixation in the combustion cylinder, oxides of nitrogen are found in the exhaust gases. Other emissions such as aldehydes may also be present.

Refineries in Los Angeles County use 130 internal combustion compressor engines which burn daily 10,500,000 c.f. of fuel gas. These have a total daily exhaust rate of 165,000 cubic feet per minute (60° F. and 1 atmosphere pressure), including 6.5 tons of hydrocarbons (mostly methane) and 4.5 tons of nitrogen oxides. Average emissions per 1,000 cubic feet of fuel gas were 1.2 pounds of hydrocarbons and 0.8 pound of nitrogen oxides. Some minor emissions of ammonia and aldehydes were reported, but the data were inconclusive.

Cooling Towers

Petroleum refineries use large quantities of water for cooling. Before the water can be reused, the heat absorbed in passing through process heat exchangers must be removed. This cooling is usually accomplished by allowing the water to cascade through a series of decks and slat-type grids in a cooling tower (fig. 8). Evaporation occurs in passing through the tower, removing sensible heat from the water.

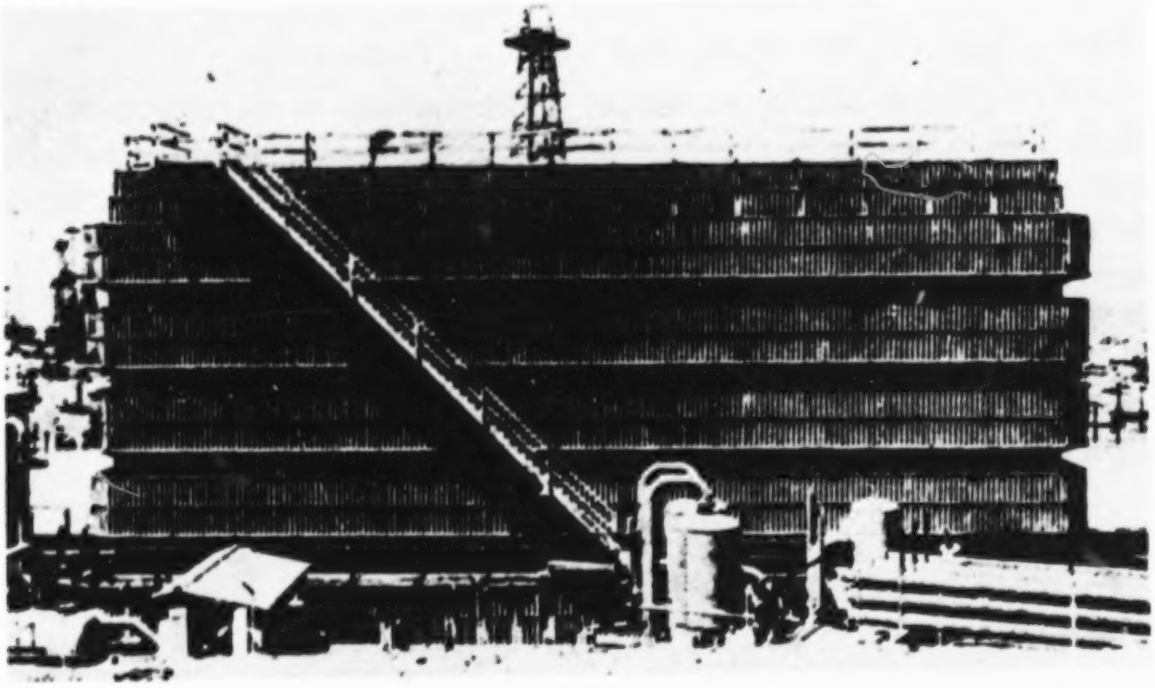

FIGURE 8. *Cooling tower*

Water which enters the tower may contain hydrocarbons from leaking heat exchangers, either dissolved or as discrete entrained globules. These hydrocarbons may escape to the atmosphere as the water passes through the cooling tower.

Oil refineries in Los Angeles County reported a total of 93 cooling towers having a combined capacity of 700,000 gallons of water per minute. The circulation rates of individual towers varied from 200 to 40,000 gallons per minute. Seventeen towers were emitting hydrocarbons totaling 3 tons per day. Individual towers emitted from 3 to 1,500 pounds per day. Emissions averaged about 9 pounds per day per 1,000 gallons per minute of water circulated.

Loading Facilities

When vessels used for the transfer of petroleum products are filled, a volume of gas is displaced equal to the volume of liquid loaded.

The displaced gas contains hydrocarbon vapors remaining from the previous filling or generated by the evaporation of the product as it is being loaded into the container.

In Los Angeles County about 90 percent of refinery output leaves the refineries through pipelines with no emission to the atmosphere. The remaining 10 percent is loaded at the refineries into tank trucks, tank cars, and containers, such as drums or barrels. Vapor recovery systems are required in Los Angeles County when loading volatile petroleum products (Reid vapor pressure greater than 4 p.s.i.a.). About 95 percent of the gasoline loaded is handled by these systems with essentially no emission to the atmosphere.

Daily emissions were calculated as 0.9 ton of hydrocarbons under the present system of controls.

Waste Water Separators and Process Drains

Some equipment and a number of operations in oil refineries may allow hydrocarbons to reach the drains and eventually the waste water separators. These include blind changing, sampling, turnarounds, leaks in process equipment, and spills. In addition, much of the water reaching the drains has been used for processing, cooling pump seals, or flushing purposes, and may already be contaminated. As the hydrocarbon-water mixture flows through the drainage system and waste water treatment plant, hydrocarbons evaporate from the surface and may escape to the atmosphere.

All major or primary oil-water separator boxes in refineries in Los Angeles County are covered or under vapor recovery. These units, 28 in number, process about 760,000 barrels of waste water daily, and recover about 3,300 barrels of slop oil a day. In addition to these main separators, final oil removal is accomplished in 68 uncovered ponds and secondary separators.

Present emissions from process drains and waste water separators were estimated at 3 tons of hydrocarbons per day.

Blowdown Systems, Including Turnarounds, Equipment Maintenance, and Flares

One of the essentials of refinery operation is the periodic maintenance and repair of equipment. This includes shutting down and starting up process units, usually called turnarounds, and the inspection, maintenance, and repair of storage tanks. Table 5 taken from Nelson (8) shows some average shutdown times for various process units.

Hydrocarbons purged during shutdowns and startups are often manifolded to blowdown systems for recovery, flaring, or, at minimum, safe venting to the atmosphere. Refineries in Los Angeles County reported a total of 382 process shutdowns in one year; 169 of these were accomplished with essentially no emission of hydrocarbon to the

TABLE 5. *Turnaround frequencies*

Units	Months of operation		Average stream time efficiency, percent
	Average	Range	
Crude and vacuum	9. 7	8. 2–13. 8	96
Thermal cracking	4. 3	3. 3– 5. 3	92
Catalytic polymerization and reforming	9. 4	7. 8–14. 0	95
Catalytic cracking	11. 6	9. 4–13. 6	94
Alkylation	13. 3	9. 3–16. 3	95
Solvent extraction	12. 9	10. 3–15. 6	94

atmosphere. The others, venting to the atmosphere or to less efficient blowdown systems, emitted varying amounts totaling about 250 tons per year, a daily average of 0.7 ton.

Storage tanks must be drained periodically for inspection and maintenance. After draining, the tanks contain hydrocarbon vapors which must be purged before workmen can enter. Emissions from this source were calculated and totaled 500 tons per year, a daily average of 1.3 tons of hydrocarbons.

All flares in refineries in Los Angeles County are the smokeless type, utilizing either steam injection or air injection (fig. 9). Sufficient information was available to determine that essentially complete combustion occurs in flares of this type, and emissions of hydrocarbon and smoke are negligible. No estimate was made of emissions of sulfur oxides, nitrogen oxides, and other possible combustion effluents.

Present emissions of hydrocarbons from blowdown systems are very minor in refineries in Los Angeles County.

Pipeline Blind Changing

In ordinary refinery operations a single pipeline connected through a manifold to a number of feeder lines may be used to carry several different products. To avoid the possibility of contaminating one product with another, it is customary to "blind off" the unused feeder lines. This is usually accomplished by loosening a flanged pipe connection, inserting a flat plate between the flanges and retightening the connection. This operation spills some of the product in the pipeline, and depending on product volatility, temperature, drainage and flushing facilities, evaporation occurs. Several devices have been developed to reduce spillage, including Hamer and Greenwood blinds (fig. 10). With highly volatile products, water or air is often forced into the pipeline to displace the product, precluding any product spillage during the change.

A 2-month record was kept of blind changing activities in refineries in Los Angeles County, including information on product volatility, amount spilled, existing drainage and flushing facilities.

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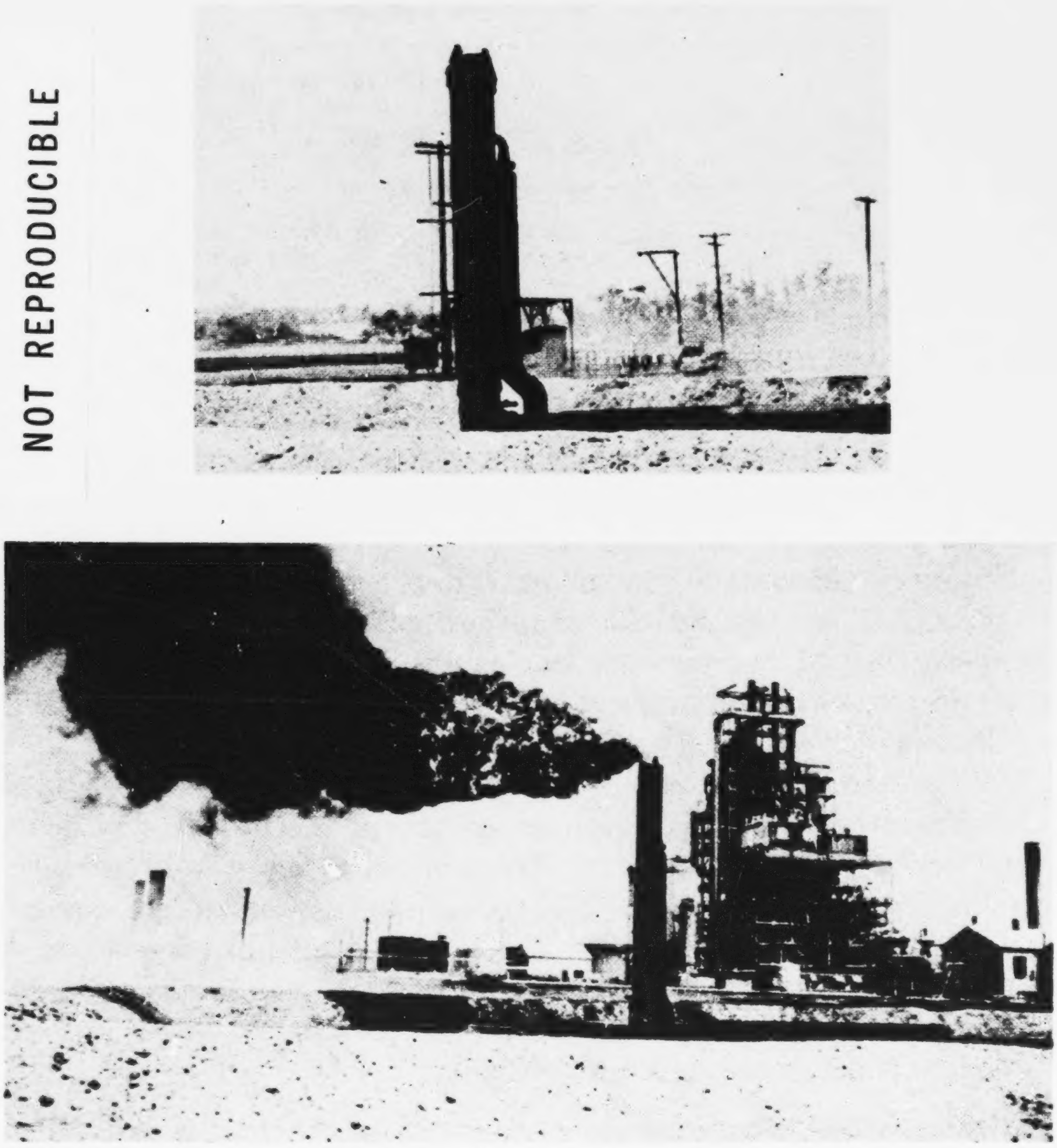

Figure 9. *Elevated flare showing the effect of steam injection*

Top, burning with steam injection
Bottom, the same installation without steam injection

During the 61-day period, over 2,500 blinds were changed, about one-half with no spillage. The other one-half spilled about 11,000 gallons of product; an estimated 2,000 gallons of this evaporated for an average daily emission of 0.1 ton of hydrocarbons.

Although never a major source of air pollution, emissions from blind changing activities have been reduced considerably in refineries in Los Angeles County by redesign of pipeline manifold systems, use of quick-change blinds, and stressing the need for immediately flushing the spilled product with water.

Boilers and Process Heaters

Many processes and operations in oil refineries necessitate the use of high pressure steam, or require feedstock at an elevated temperature. A wide variety of boilers and process heaters are used to fill

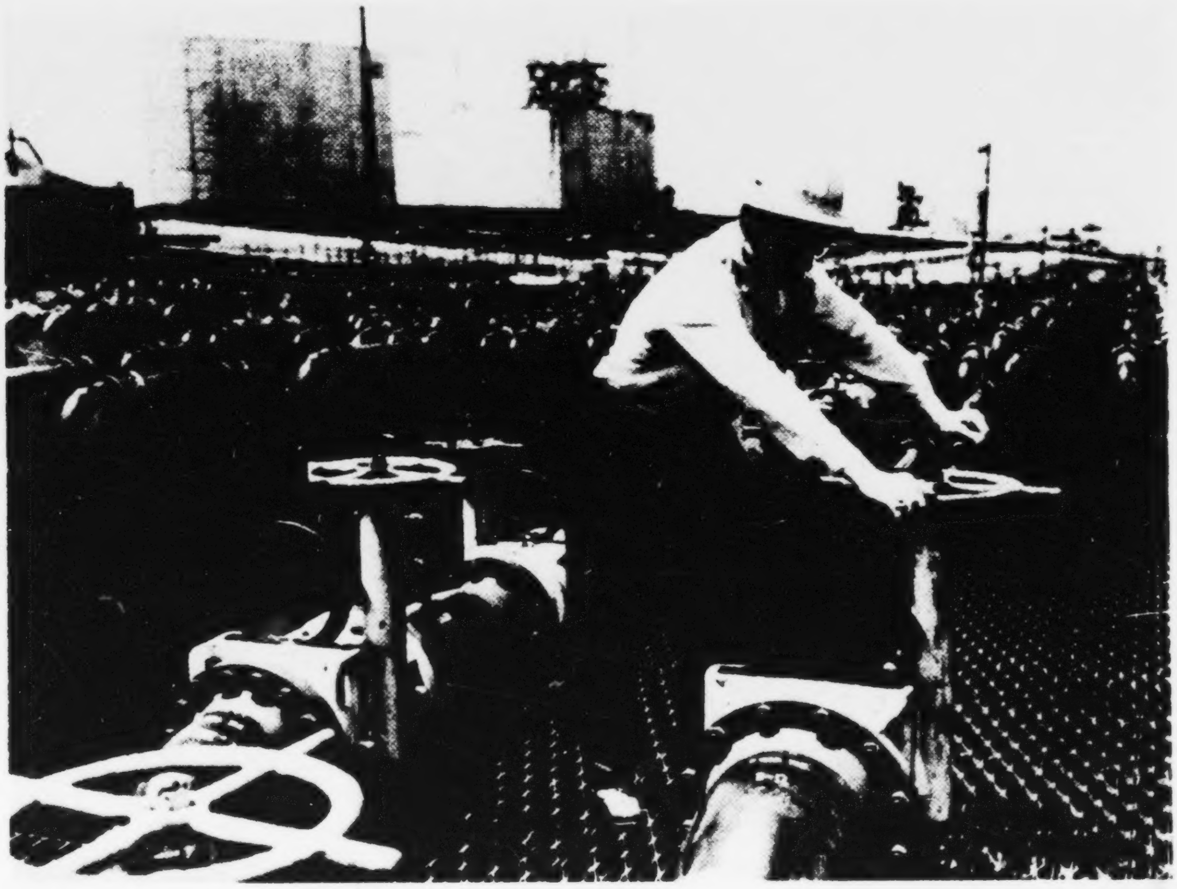

FIGURE 10. *Main oil transfer area showing manifolds equipped with Hamer blinds in the foreground*

these needs. Heaters may be of unique design, although most units are the box-type shown in figure 11, or the cylindrical, vertical-type illustrated in figure 12. Boilers are generally of conventional design. The fuel may be refinery gas, natural gas, heavy fuel oil, coke, or combinations depending on economics and operating conditions.

In the Joint Project study, sulfur emissions were calculated from the sulfur content of the fuels burned. Average emissions of the other combustion products, as well as the SO_3/SO_2 ratio were determined by field tests on 14 heaters and 10 boilers. These results are shown in table 6.

Vacuum Jets

Most refineries operate some process equipment at less than atmospheric pressure. A steam-driven vacuum jet or ejector (fig. 13), sometimes coupled with a barometric condenser, frequently is used to produce and maintain a vacuum in refinery process equipment. Light hydrocarbons which do not condense in the barometric condenser are discharged with the exhaust steam.

Discharges from vacuum jets in refineries in Los Angeles County have been completely controlled by venting exhaust lines to a fume burner or to fireboxes on boilers and heaters.

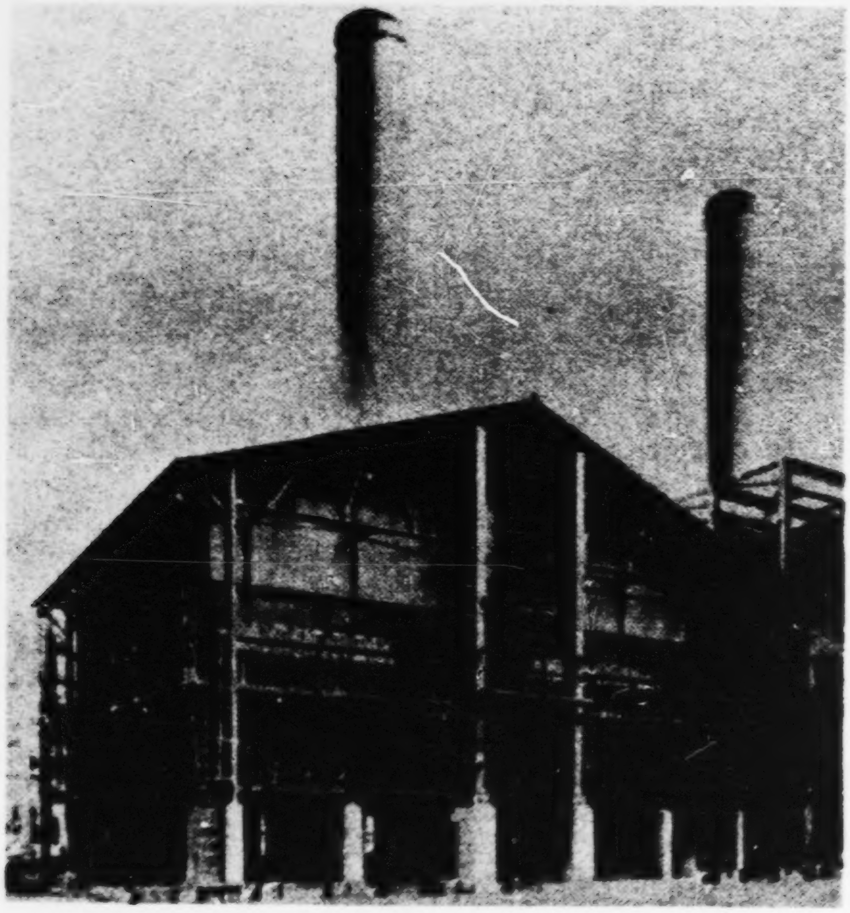

FIGURE 11. *A conventional box-type heater*

TABLE 6. *Emissions from boilers and process heaters in Los Angeles County refineries*

Emission	Average emissions		Total emissions from refineries in Los Angeles County, tons per day
	Fuel gas, pounds per 1,000 cu. ft.	Fuel oil, pounds per gallon	
Oxides of nitrogen, as NO_2	0.23	0.068	46
Aldehydes, as HCHO	0.0031	0.0006	0.5
Hydrocarbons, as hexane	0.026	0.0034	5
Organic acids, as acetic acid	0.014	0.011	3.5
Particulate matter	0.021	0.020	5
Sulfur dioxide			*72
Sulfur trioxide			**2

*Calculated from sulfur content of fuel.

**Ratio of SO_3 to total S as SO_2 averaged 0.03.

Sampling

The operation of process units is constantly checked throughout the refinery by routine analyses of feedstocks and products. To obtain representative samples for these analyses, sampling lines must be purged, resulting in possible hydrocarbon vapor emissions. Emissions from this source have been reduced in refineries in Los Angeles County by installation of drains and water flushing facilities at sampling points, and by employee educational programs. This source

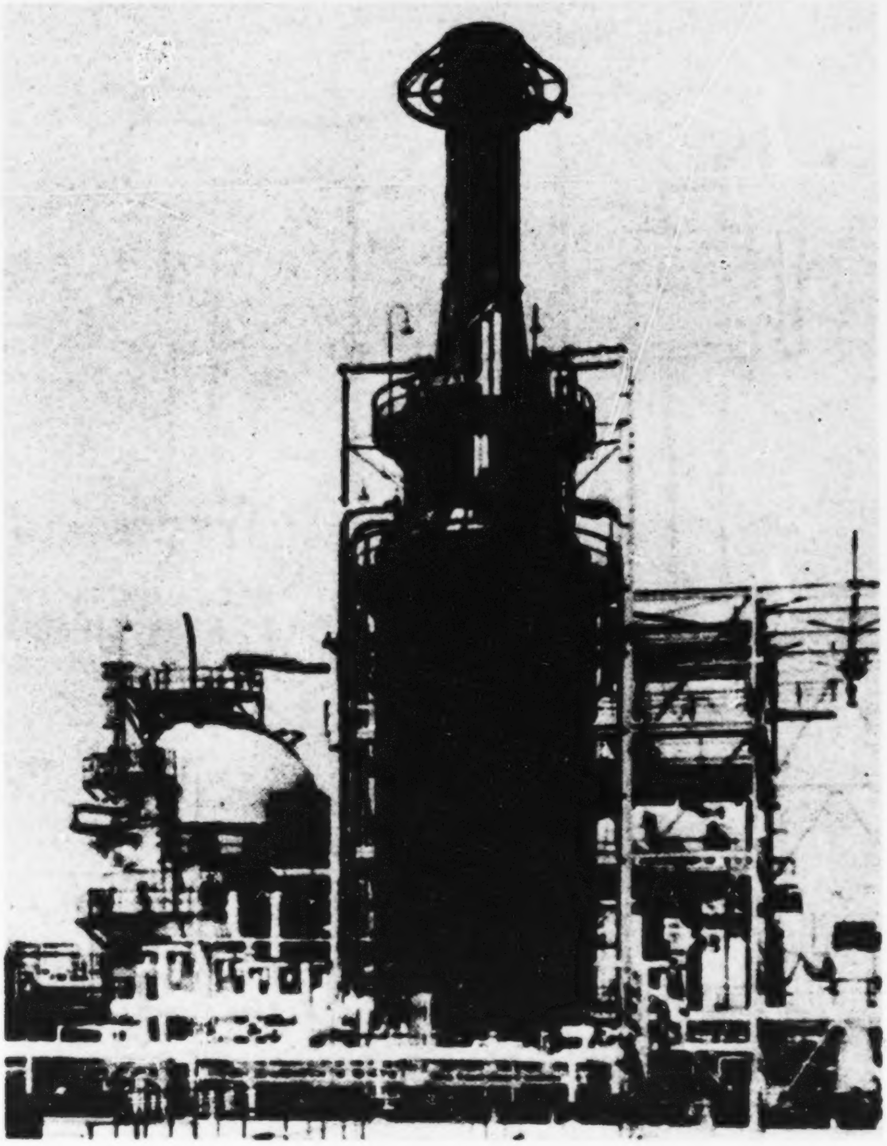

FIGURE 12. *A vertical, cylindrical heater*

was not studied by the Joint Project; however, an estimation of emissions from refineries in Los Angeles County is available and indicates an emission of 0.8 ton of hydrocarbon daily from sampling operations (9).

Air Blowing

In some refineries air is blown through petroleum products for brightening (removal of turbidity due to moisture), for agitation during treating operations, and during asphalt processing. The effluent air may contain hydrocarbon vapors and mists, and malodorous compounds. Also, air or steam blowing is used to oxidize or strip spent chemicals or catalysts in various treating operations, with possible emissions of sulfur oxides, hydrocarbons, odors, and other materials.

Air blowing is a minor operation used intermittently at three refineries in Los Angeles County.

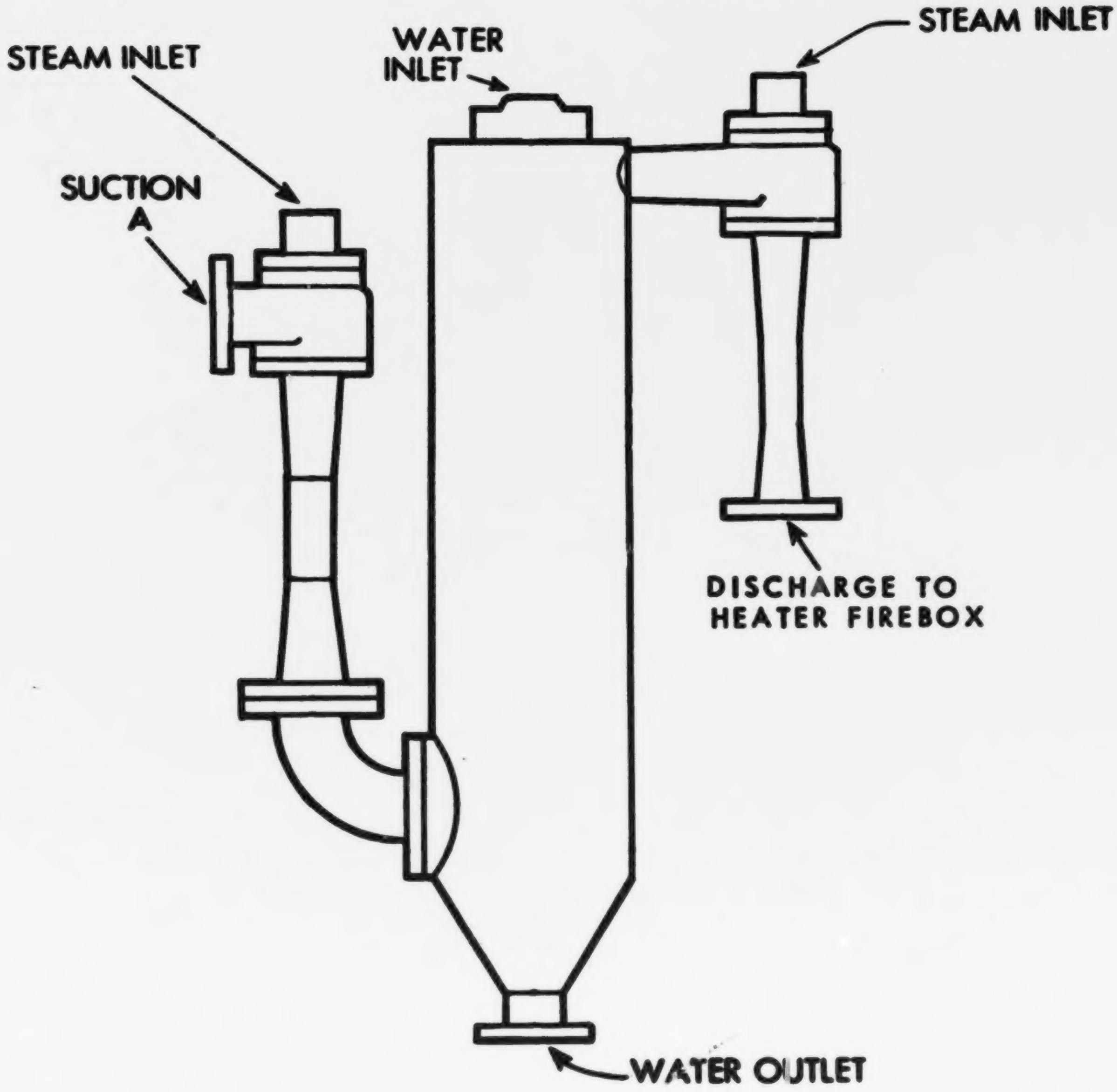

FIGURE 13. *Schematic drawing of a two-stage, steam ejection, vacuum jet*

Acid Treating

The operation of acid treating units, including acid concentrators and the disposal of acid sludge, may include sources of sulfur oxide emissions as well as of small amounts of hydrocarbons. The amount of sulfur oxides released will vary widely depending on the amount of acid used, products treated, and methods of acid concentration and acid sludge disposal. Emissions from these sources have been essentially eliminated in refineries in Los Angeles County, and were not studied by the Joint Project.

Control of Emissions From Oil Refineries

Although this manual is a survey manual and not primarily directed toward the problem of control, a general discussion of this aspect of refinery emissions is desirable. Control can be accomplished by three methods: process changes, installation of control equipment, and improved housekeeping, usually involving employee education and better maintenance. Combinations of these methods often prove the most practical solution to an air pollution problem. A list of possible control techniques for most sources in oil refineries is presented in appendix II.

Process Changes

Some sources of atmospheric emissions can best be controlled by changing refining methods or altering the operation of the refining equipment. Typical examples of process changes which eliminate or reduce emissions include improved procedure for equipment shutdowns and startups, piping changes to eliminate blinds, substitution of catalytic hydrogen treating for chemical treating, use of harder catalysts to reduce attrition losses, and product shipping by pipeline rather than by tank truck or tank car. Some of these process changes are an integral part of normal refinery modernization and improvement; others may become economically feasible when compared with the cost of installing air pollution control equipment.

Control Equipment

Common methods of reducing air pollution include installation of equipment to remove contaminants from emissions and facilities to decrease the volume of emissions. Control equipment in refineries may include floating roofs for storage tanks, covers for waste water separators, high-efficiency dust removal equipment on catalytic cracking units, waste heat boilers on catalyst regenerators, smokeless flares, vapor recovery systems, and sulfur recovery plants.

Improved Housekeeping

Improved housekeeping, including maintenance and employee education, is often a very practical method for alleviating odor problems and reducing hydrocarbon emissions. It is often the only practical control method for some sources, such as pipeline valves, pump seals, and sampling operations. For nearly all sources, especially process drains, waste water separators, treating units, blind changing, and loading operations, employee awareness of the air pollution problem will reduce emissions.

Economics of Control

The economics of air pollution control can be determined only for individual refineries and for specific sources within the refinery. The cost of control is a function of the accumulated capital investment for equipment, amortization time, and interest rates. It is also a function of maintenance and other operating expenses. However, the amount of money spent is a very poor measure of accomplishment in air pollution control. Frequently, oil refineries have been required to spend large sums to meet arbitrary limits in regulations which are not based on sound technical data giving reasonable assurance of benefits commensurate with costs. In some cases, control equipment has a "payout," but in more cases, especially control of odor and particulate emissions, the dollars spent are never fully returned (10). Air pollution control activities may improve plant safety, employee morale, and community relations.

A plant which was well designed when built may not require additional capital expenditures for emission control for many years. On the other hand, in a less carefully built plant or in one where new processes have been added, it may be necessary to spend large sums to achieve comparable control.

Estimation of Atmospheric Emissions From Oil Refineries

Many factors must be considered before an attempt is made to apply the results of the Los Angeles refinery studies to other refineries. The types of crude run and the processes used must be considered. The status of control efforts in the refinery in question must be appraised. Comparisons of emissions from one refinery with emissions from another on the basis of refining capacity or fuel consumption can be grossly misleading. When an estimate of emissions is required, judgment must be used in evaluating the foregoing factors.

The most reliable estimate of emissions from oil refineries should be based on on-site test results, particularly for sources with highly variable emission rates such as evaporation from tankage, catalytic cracking regenerators, air blowing, blowdown systems, and vacuum jets. However, for many sources, field testing programs are complicated, time-consuming, and expensive, and may not be practical for estimation of gross emissions. In such cases, average on-site test data obtained from other refinery studies may be used to prepare a rough estimate of emissions. The estimates so obtained may have large inherent errors, and should not be used as the sole basis for conclusions or recommendations relating to regulations. Nor should the estimates be used as a basis for requiring installation of control facilities.

Emission factors calculated from the Los Angeles survey are reported herein. Where a range of values is presented, the low value represents a figure derived from recent surveys of Los Angeles plants. The high values are rough estimates of the emissions in the Los Angeles area before the extensive control programs were inaugurated. It should be recognized that in most instances these high values are only educated guesses with limited measurements to substantiate the figures.

The data from the Los Angeles survey were used to calculate two factors for some sources of emissions: one based on the easily obtained refinery capacity data, and a second based on the number of units such as valves or pump seals in the refinery.

Refinery air pollution surveys may be necessary for a number of purposes, and the survey method should be consistent with the intended use of the estimated figures. It would be wasteful to make extensive calculations and perhaps run field tests when only a rough estimate of emissions is required, and rash to expect an accurate, reliable result from a few simple calculations based on refinery capacity. This section presents two methods for approximating emissions from oil refineries: a very rough estimate of gross hydrocarbon emissions based essentially on refinery capacity, and an approximation involving calculations based on detailed refinery information and the Los Angeles refinery experience for specific emission sources. These are two examples of possible uses of Joint Project data. The best type of refinery survey must be determined for each case, depending on the time and refinery information available, and the expected use of the survey.

First Estimate of Gross Hydrocarbon Emissions

A very rough estimate of total hydrocarbon emissions may be made using information concerning refinery capacity, including vacuum distillation and catalytic cracking capacities, and some knowledge of the status of the control program in effect. Table 1 gives refinery capacities and the capacities of various processes summarized by States. Similar information for every refinery in the United States and Canada is available in the literature (4). The status of emission control must be evaluated individually for each refinery or area being surveyed. Generally, initial control efforts are directed against SO_2, smoke, dust, and other more noticeable forms of air pollution. The magnitude of programs to control emissions is usually dictated by refinery location, proximity of urban areas, and geographical and meteorological conditions.

Hydrocarbon emissions from petroleum refineries may range from 0.1 to 0.6 percent by weight of the crude throughput. The lower value is applicable to refineries practicing extensive hydrocarbon control activities, and may seldom be found outside Los Angeles County. The higher value may be found at refineries where stringent control of hydrocarbon emissions is not practiced. Both values refer to refineries with nearly complete processing schemes. Smaller refineries practicing only crude topping, treating, and blending will tend toward the lower values.

Table 7 shows factors proposed for making a gross estimate of hydrocarbon emissions. Ranges of values have been given for those sources from which emissions may vary greatly. The values and ranges shown are based on the best data available from refineries in Los Angeles County before inauguration of hydrocarbon control programs and after application of these programs. The preceding section of this manual details the control measures used by the Los Angeles refineries to achieve these lower values.

The following example illustrates the use of table 7 for estimating gross hydrocarbon emissions. Assume a 20,000 barrel per day refinery, with vacuum distillation and catalytic cracking units of 6,000 barrels per day capacity each. Further assume that control efforts have been directed toward storage and blowdown systems, and assign midrange factors to these sources. The higher factors should probably be used for separators and vacuum jets since controls on the sources may not have been applied. Table 8 illustrates the calculation of hydrocarbon emissions for this hypothetical case.

TABLE 7. *Hydrocarbon emission values, Los Angeles survey*

Source	Emission factors		
	Units	Value	Possible range of values*
Storage tanks	Pounds per 1,000 barrels refinery capacity		100–1,000
Blowdown systems	Pounds per 1,000 barrels refinery capacity		5– 350
Waste water separators	Pounds per 1,000 barrels refinery capacity		10– 200
Leakage (valves, pumps, etc.)	Pounds per 1,000 barrels refinery capacity	60	
Others (loading, cooling towers, boilers, blind changing, etc.)	Pounds per 1,000 barrels refinery capacity	150	
Catalytic cracking unit regenerators	Pounds per 1,000 barrels fresh feed rate	170	
Vacuum jets	Pounds per 1,000 barrels vacuum distillation		0–130

*Range indicates average emissions for refineries in Los Angeles County before inauguration of special air pollution control programs, and at present, with extensive controls.

TABLE 8. *Sample calculation of hydrocarbon emissions—first estimate*

Source	Refinery or process capacity, 1,000 barrels/day	Emission factor, pounds per 1,000 barrel capacity	Emissions pounds/day
Storage	20	500	10,000
Blowdown system	20	200	4,000
Waste water separator	20	250	5,000
Leakage	20	60	1,200
Other	20	150	3,000
Catalytic cracker	6	170	1,000
Vacuum distillation	6	130	800
Total loss			25,000

This is about 12 tons daily, amounting to $\frac{12\times 2{,}000}{20{,}000\times 300}\times 100=0.4$ percent of crude throughput.

Detailed Survey of Atmospheric Emissions From Oil Refineries

The procedure outlined below makes full use of average emission data, and will allow an estimate of emissions from nearly every significant source in oil refineries. This method requires the cooperation of the refinery or refineries being surveyed. Detailed information must be obtained on process capacities, fuel requirements, production figures, and result of sulfur analyses.

The indicated emission factors for various sources should not be considered absolute values, but, where possible, should be used in conjunction with refinery inspections and available refinery emission data. This manual includes much information on the control measures and refinery process schemes incorporated into the emission factors. This information should be compared with the refinery being surveyed for a realistic interpretation of the emission factors presented here.

Emissions of Sulfur Oxides

Emissions of sulfur oxides are a function of the sulfur content of the crude oil being processed, and do not lend themselves to estimates based on average values for other refineries. However, a knowledge of the distribution of sulfur throughout the plant is important to the refiner to attain maximum process efficiency and product quality, and, if available, these data can be used to make a gross sulfur balance for the refinery.

Sulfur enters the refinery in the crude oil, in purchased fuel oil or gas, and as sulfuric acid used in various processes. Most of this sulfur routinely leaves the refinery in the various products, as spent sulfuric acid shipped out for regeneration, as sulfides or sulfates in the liquid wastes, or is recovered in sulfur recovery plants. The difference will be emitted to the atmosphere mainly as sulfur dioxide, although some SO_3 and H_2S may be released.

Miscellaneous Combustion Emissions

Along with the SO_2 and hydrocarbons, oil refineries emit carbon monoxide, nitrogen oxides, aldehydes, organic acids, ammonia, and particulate matter. These are discharged from combustion sources, including catalyst regeneration units, boilers and process heaters, and compressor internal combustion engines. Tables 9 and 10 give factors for combustion emissions, excepting sulfur oxides and hydrocarbons, based primarily upon the Los Angeles refinery studies.

TABLE 9. *Factors for particulate emissions*

Source	Units of factor	Value
Boilers and process heaters	Pounds per 1,000 cu. ft. of fuel gas burned	0.02
	Pounds per barrel of fuel oil burned	.8
Fluid catalytic units:		
With electric precipitation	Percent of catalyst circulated	.0009
Without electric precipitation	Percent of catalyst circulated	.005
Moving-bed catalyst units, high efficiency centrifugal separators.	Percent of catalyst circulated	.002

Hydrocarbon Emissions

Calculated Emissions From Storage Tanks and Loading Operations

Hydrocarbon emissions from storage tanks and product loading operations can be calculated directly. These emissions accounted for about one-half the total hydrocarbon emissions from the Los Angeles refineries during the survey.

TABLE 10. *Factors for emissions of nitrogen oxides, carbon monoxides, aldehydes, and ammonia from oil refineries*

Source	Units of factor	Value of factor for various emissions			
		NO_x as NO_2	CO	Aldehydes as HCHO	Ammonia as NH_3
Boilers and process heaters	Pounds per 1,000 cu. ft. of fuel gas burned.	0.23	Neg.	0.0031	Neg.
	Pounds per barrel of fuel oil burned.	2.9	Neg.	.025	Neg.
Compressor internal combustion engines.	Pounds per 1,000 cu. ft. of fuel gas burned.	.86	Neg.	.11	0.2
Fluid-bed catalytic cracking units.	Pounds per 1,000 barrels of fresh feed.	63	13,700	19	54
Moving-bed catalytic cracking units.	Pounds per 1,000 barrels of fresh feed.	5.0	3,800	12	5.0

A method of calculating emissions from fixed roof and floating roof storage tanks is presented in appendix I, along with a typical calculation sheet. This method is presented in greater detail, including nomographs to simplify calculations, in publications of the American Petroleum Institute (7), and the Los Angeles County Air Pollution Control District (11). This method of calculation is now in process of modification. Reference should be made to API Bulletins 2512, 2513, and others planned for future release. Pressure storage tanks and storage tanks connected to vapor recovery systems, if operated correctly, will have negligible losses.

Losses from product loading into tank cars and tank trucks can be calculated using the following formula:

$$F = 0.063\,PV$$

where

F = weight of hydrocarbon vapors vented, pounds.

P = partial pressure at 60° F. of the hydrocarbon vapors in the air-vapor mixture (usually considered to be the true vapor pressure of the liquid remaining in the vessel before filling), pounds per square inch absolute.

V = volume of product loaded, barrels.

The derivation of this formula is based on the following assumptions:

1. The hydrocarbon vapors vented occupy 6 cubic feet per pound.

2. The volume of gases vented is equal to the volume of liquid loaded.
3. The displaced gases are saturated with hydrocarbon vapors.
4. The hydrocarbon vapor-air mixture conforms to Dalton's law of partial pressures.

Hydrocarbon Emissions From Combustion Sources

In most refineries combustion operations are not a major source of hydrocarbon emissions. Table 11 presents average factors for combustion sources.

Table 11. *Factors for hydrocarbon emissions from combustion sources*

Source	Units of factor	Value
Boilers and process heaters	Pounds per 1,000 cubic feet of fuel gas burned.	0.026
	Pounds per barrel of fuel oil burned	.14
Fluid catalytic cracking units	Pounds per 1,000 barrels fresh feed	220
Moving-bed catalytic cracking units	Pounds per 1,000 barrels fresh feed	87
Compressor internal combustion engines	Pounds per 1,000 cubic feet of fuel gas burned.	1.2

Hydrocarbon Emissions From Equipment Leaks

Four types of equipment—pumps, compressors, pipeline valves, and pressure relief valves—may leak hydrocarbons to the atmosphere. Factors for these sources should be given as the average for a particular type of equipment in a specific service, such as mechanical pump seals handling L.P.G., or pressure relief valves on storage tanks. However, detailed information on the number and distribution of this equipment is seldom available, so two factors for each source are presented in table 12. One is based on the number of units, and a second factor is based on the easily obtained refinery capacity. While both factors are subject to error, the second factor is less reliable.

Emissions from these leak sources are strongly affected by the degree of maintenance in the refinery. The factors presented for average

Table 12. *Factors for hydrocarbon emissions from equipment leakage*

Source	Units of factor	Value
Pipeline valves	Pounds per day per valve	0.15
Vessel relief valves	Pounds per day per valve	2.4
Pipeline relief valves		Neg.
Pump seals	Pounds per day per seal	4.2
Compressor seals	Pounds per day per seal	8.5
Pipeline valves	Pounds per 1,000 barrels refinery capacity	28
Vessel relief valves	Pounds per 1,000 barrels refinery capacity	11
Pump seals	Pounds per 1,000 barrels refinery capacity	17
Compressor seals	Pounds per 1,000 barrels refinery capacity	5

unit emissions reflect the high degree of maintenance demanded of refineries in Los Angeles County. The factors based on refinery capacity are for complete refineries with extensive processing equipment. It has been assumed that maintenance is the only control activity used on these leak sources. In practice, some refineries may vent some of their pressure relief valves and compressor seals to blowdown systems, and the factors based on refinery capacity should be reduced in these cases.

Hydrocarbon Emissions From Other Process Equipment

Emissions from many sources in oil refineries are strongly affected by existing control programs, and make the use of average data from Los Angeles County refineries precarious. A few of these may be major sources of hydrocarbon emissions, and an estimate of the effectiveness of existing control measures is necessary before an average factor can be selected. The range of factors for these sources is derived from the survey of emissions from refineries in Los Angeles County. The lowest values assume the use of the control techniques described in previous sections, whereas the higher value is based on rough estimates of the emissions that may have occurred from the same refineries before the extensive control programs were initiated.

Factors for emissions from process equipment are shown in table 13. The "other" source includes air blowing, blind changing, and sampling.

TABLE 13. *Factors for hydrocarbon emissions from miscellaneous process equipment*

Source	Units of factor	Value	Range of values
Blowdown systems	Pounds per 1,000 barrels refining capacity	----------	5–300
Process drains and waste water separators.	Pounds per 1,000 barrels waste water processed	----------	8–210
Vacuum jets	Pounds per 1,000 barrels vacuum distillation capacity.	----------	0–130
Cooling towers	Pounds per million gallons cooling water circulated.	6	----------
Other	Pounds per 1,000 barrels refinery capacity	10	----------

In concluding it should be emphasized that the methods for estimating emissions presented in this manual are not a substitute for actual testing work. Because of differing maintenance, process methods, crude sources, control measures, and other factors, the use of average data can give only a very rough indication of the magnitude of emissions. When a reliable estimate is needed, survey work must be carried out. The procedures suggested in this manual will be of greatest value when used in conjunction with available refinery test data and actual surveys on the most significant sources of emissions.

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Appendices

I—Method for Calculating Hydrocarbon Vapor Losses From Storage Tanks.
II—Control Methods.
III—Glossary of Terms Used in Petroleum Refining.

Appendix I

Method for Calculating Hydrocarbon Vapor Losses From Storage Tanks

Many methods for calculating hydrocarbon losses from storage tanks have been developed by various groups from experimental studies. The method described below was used by the Joint Project and is presented in greater detail in the literature (7) (11), including nomographs to simplify calculations.

The equations used for making the calculations are as follows:

1. *Breathing Losses From Fixed Roof Tanks*

$$B=\frac{PD^{1.8}}{14.5}F_oF_p$$

2. *Filling Losses From Fixed Roof Tanks*

$$F=\frac{3PV}{10{,}000}K_t$$

3. *Evaporation Losses From Floating Roof Tanks*

$$E=CPD$$

4. *Filling Losses From Floating Roof Tanks*

$$F_e=\frac{V}{10{,}000}$$

Where:

B=breathing loss from a fixed roof tank, in barrels per year.
F=filling loss from a fixed roof tank, in barrels per year.
E=evaporation loss from a floating roof tank, in barrels per year.
F_e=filling loss from a floating roof tank, in barrels per year.
P =true vapor pressure at the average liquid body temperature, in pounds per square inch absolute.

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D = tank diameter, in feet.

V = volume of liquid product added to the tank, in barrels per year (in the case where product is being withdrawn *simultaneously* with product addition, V is the excess of addition over withdrawal).

F_o = outage factor for fixed roof tanks.

F_p = paint factor for fixed roof tanks.

K_t = throughput factor.

C = floating roof factor for type of shell construction, seal, and roof.

Values to be used for the outage, paint, throughput, and floating roof factors are:

1. *Outage Factor, F_o*

$$F_o = \frac{1}{5.7}(H+5)^{0.57} - 0.1$$

Where H = outage, or height between top angle of the tank and the liquid surface, in feet.

A table of outages versus outage factors prepared from the equation is as follows:

H	*F_o*
1	0.39
5	0.55
10	0.72
15	0.87
20	1.00
25	1.12
30	1.23
35	1.33
40	1.43
45	1.53
50	1.62

Some adjustments may have to be made to the outage value used if the volume under the tank roof is much different from the volume under a conical roof with a pitch of ¾ inch per foot. A larger volume will call for a higher outage, and a lower volume a lower outage.

2. *Paint Factor, F_p*

Paint	*F_p*
Chalking white	0. 75
Aluminum	1. 00
Light gray	1. 10
Black, no paint, or needs repainting	1. 25

3. *Throughput Factor, K_t*

Tank turnovers per year	K_t for general refinery service	K_t for marketing plants and terminals
0–10	1.00	1.00
12	.91	1.00
15	.75	1.00
20	.59	1.00
25	.50	1.00
30	.47	1.00
40	.44	1.00
40–60		.80
60–100		.50

4. *Floating Roof Factor, C*

Shell construction	Seal	C
Welded	Single or double	0.49
Riveted	Double	.56
Riveted	Single	1.20

The equations for fixed roof tanks are based on the following assumptions:

a. Roofs are vapor-tight.
b. Vents, gauge hatches, and other accessories are vapor-tight.
c. Tanks operate at essentially atmospheric pressure; i.e., with vent pressure and vacuum settings in the order of 0.5 ounce per square inch.
d. The volume under the roof is essentially the same as the volume under a low pitch conical roof having a slope of ¾ inch per foot.
e. The mean daily temperature change is 16° F.

The equations used for estimating losses from floating roof tanks are based on the following assumptions:

a. Average wind velocities are 5 to 10 miles per hour.
b. Tanks are in good condition.
c. Tank shells and roofs are painted aluminum or gray.
d. Tanks are 8 to 20 years old and have sealing rings of the type which were in use at the time of their construction.

Calculation Sheet—Emissions From Fixed Roof and Floating Roof Tanks*

Table of data and assumptions

1. Product ______ ______
2. Reid Vap. Press ______ lbs.
3. Avg. Stge. Temp ______ °F
4. True Vap. Press., (P) ______ p.s.i.a.
5. Tank Diam., (D) ______ ft.
6. Avg. Outage ______ ft.
7. Outage Factor, (F_o) ______
8. Paint Factor, (F_p) ______
9. Throughput, (V) ______ bbls/yr.
10. Turnovers per year ______
11. Throughput Factor, (K_t) ______
12. Type F.R. Seal ______
13. Shell Construction ______
14. F.R. Evap. Factor, (C) ______
15. Density of Condensed Vapors (W) ______ lbs/bbl.

I. LOSSES FROM FIXED ROOF TANKS

1. BREATHING LOSS: $B=\frac{PD^{1.8}}{14.5}F_oF_p\times\frac{W}{365}=$ =______lbs/day

or from Nomograph: $B=\text{——}\ \frac{bbl}{yr}\times\frac{W}{365}=$ =______lbs/day

2. FILLING LOSS: $F=\frac{3PV}{10000}K_t\times\frac{W}{365}=$ =______lbs/day

or from Nomograph: $F=\text{——}\ \frac{bbl}{yr}\times\frac{W}{365}=$ =______lbs/day

3. TOTAL FIXED ROOF LOSSES=BREATHING LOSS+FILLING LOSS =______lbs/day

II. LOSSES FROM FLOATING ROOF TANKS

1. EVAPORATION LOSS: $E=C_sP_sD_s\times\frac{W}{365}=$ =______lbs/day

2. FILLING LOSS: $F=\frac{V}{10000}\times\frac{W}{365}=$ =______lbs/day

3. TOTAL FLOATING ROOF LOSSES=EVAPORATION LOSS+FILLING LOSS =______lbs/day

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*Taken from Lunche and Deckert, "Hydrocarbon Losses from Petroleum Storage Tanks," Los Angeles County Air Pollution Control District (December 1956).

Appendix II

Control Methods

1. Storage—
    - A. Connect to vapor recovery systems.
    - B. Floating roofs.
    - C. Pressure tanks.
    - D. Connect to gas holder (vapor balance).
2. Catalyst regenerators—
    - A. High-efficiency separators on flue gas stack.
    - B. Maintain slight vacuum on catalyst elevators and vent exhaust to separators.
    - C. Vent exhaust from airlift catalyst systems to separators.
    - D. Waste heat boiler to burn CO and hydrocarbons.
3. Pipeline valves—
    - A. Inspection and maintenance.
4. Pressure relief valves—
    - A. Manifold to vapor recovery system or flares.
    - B. Rupture discs in addition to relief valves.
    - C. Dual valves with shut-offs.
    - D. Inspection and maintenance.
5. Pump and compressor seals—
    - A. Mechanical seals on pumps in difficult service.
    - B. Sealing glands with oil under pressure.
    - C. Venting glands to vapor recovery system.
    - D. Inspection and maintenance.
6. Loading facilities—
    - A. Vapor collection equipment.
    - B. Careful operation to decrease spillage.
    - C. Subsurface loading arms.
7. Drains and waste water separators—
    - A. Enclosing initial separator boxes.
    - B. Cover sewer junction boxes.
    - C. Good housekeeping to reduce spillage to sewer.
    - D. Liquid seals in drains.
8. Blowdown systems—
    - A. Smokeless flares.
    - B. Vapor recovery systems, usually a gas holder, gas compressor, and discharge to refinery fuel gas system or absorber unit.

9. Turnarounds—
   - A. Depressurizing and purging to vapor recovery prior to opening vessels.
   - B. Depressurizing and water displacement to vapor recovery prior to opening vessels.
10. Boilers and process heaters—
   - A. Electronic smoke indicators.
   - B. Maintain proper operating conditions.
   - C. Use of gaseous fuel where possible in place of fuel oil.
   - D. Removal of hydrogen sulfide and mercaptans from fuel gas.
11. Vacuum jets—
   - A. Venting to a boiler or heater firebox.
12. Acid treating—
   - A. Convert batch-type agitators, which use air blowing, to continuous treating with mechanical mixing.
   - B. Replace hydrolysis-concentration method of acid recovery with acid regeneration technique.
   - C. Replace acid sludge combustion with methods involving dumping or chemical destruction.
   - D. Vent gases generated by acid sludge storage and shipping to caustic scrubber to remove SO_2 and malodors, and to firebox to burn hydrocarbons and malodors.
   - E. Replace acid treating units with catalytic hydrogenation units.
13. Doctor treating—
   - A. Steam stripping of spent doctor solution to remove and recover hydrocarbons prior to air blowing for regeneration.
   - B. Burning effluent from air blowing.
14. Noxious gases from sour water strippers—
   - A. Recovery of H_2S and ammonia by conversion to salable products.
   - B. Oxidize by converting sulfides to thiosulfates.
15. Spent caustic disposal—
   - A. Venting stripping effluent gases through furnace fireboxes.
16. Mercaptan disposal—
   - A. Convert to disulfides.
   - B. Use of mercaptans in organic synthesis.
   - C. Combustion in furnace fireboxes.
17. Recovery of H_2S from sour gases—
   - A. Collection by liquid absorption, and conversion to sulfur or sulfuric acid by refinery or others.
18. Fume disposal from air blowing operations—
   - A. Incineration.
   - B. Scrubbing.

Appendix III

Glossary of Terms Used in Petroleum Refining[1]

A

absorption oil—An oil of high affinity for the light hydrocarbons, but containing few or none of the light compounds composing gasoline and natural gas.

absorption plant—A plant for recovering the condensable portion of natural or plant gas, by absorbing these heavier hydrocarbons in an absorption oil (often under pressure), followed by separation and fractionation of the absorbed material.

accumulator—A vessel for the temporary storage of a gas or liquid; usually used for collecting sufficient material for a continuous charge to some refining process.

acid sludge—The residue left after treating petroleum oil with sulfuric acid for the removal of impurities. It is a black, viscous substance containing the spent acid and the impurities which the acid has separated from the oil.

acid treatment—An oil-refining process in which unfinished petroleum products, such as gasoline, kerosine, diesel fuel, and lubricating stocks, are contacted with sulfuric acid to improve color, odor, and other properties.

alicyclic hydrocarbons—Hydrocarbons which contain a ring of carbon atoms but do not belong to the aromatic series.

aliphatic hydrocarbons—Hydrocarbons of open-chain structure such as ethane, butane, octane, butene, acetylene.

alkylation—Formation of complex saturated molecules by direct union of a saturated and an unsaturated molecule.

API—American Petroleum Institute.

API gravity—An arbitrary scale expressing the gravity or density of liquid petroleum products. The measuring scale is calibrated in terms of "API" degrees. It may be calculated in terms of the following formula:

$$\text{deg API} = \frac{141.5}{\text{sp gr } 60/60\ \text{F}} - 131.5$$

aromatic compounds—Those derived from benzene with one or more benzene rings of carbon atoms as distinct from those of aliphatic or alicyclic character.

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[1] Taken from API Manual "Glossary of Terms Used in Petroleum Refining," 1953.

aspirator—An apparatus which serves to create a partial vacuum through pumping a jet of water, steam, or some other fluid or gas past an orifice opening out of the chamber in which the vacuum is to be produced.

B

barometric condenser—A device which, by condensing steam, produces a partial vacuum in a piece of refinery equipment, such as a vacuum pipe still.

barrel—As the standard unit of measurement of liquids in the petroleum industry, it contains 42 U.S. standard gallons.

base stocks[2]—Any oil fraction which has been refined for use as a component in a finished product.

batch still—A petroleum still in which the distillation is carried out in "batches," the entire still charge being introduced before the fires are lighted, and the distillation being completed without the introduction of an additional charge.

benzene—This is an old term for light petroleum distillates covering the gasoline and naphtha range.

blended fuel—Fuel oil which is a mixture of two or more types (residual, distillate, or cracked fuel).

blowdown stack—A stack set upon a small tank into which the contents of a unit are emptied when an emergency arises. Connections are usually made so that steam can be injected into the tank to prevent ignition of the material therein. Also water quench is frequently provided to reduce the amount of oil vapors issuing from the stack.

blowing—Agitating a liquid by the introduction of compressed air near the bottom of the tank or container. In "blowing bright," the air assists in carrying off moisture, whereas, in acid treating, the air is used only for agitation.

bottoms—The liquid which collects in the bottom of a vessel, either during a fractionating process or while in storage (tower bottoms, tank bottoms).

breathing—The movement of gas (oil vapors or air) in and out of the vent lines of storage tanks due to alternate heating and cooling.

bright—The term applied generally to lubricating oils, meaning clear or free from moisture.

bubble tower or column—A fractionating tower so constructed that the vapors rising pass up through layers of condensate on a series of plates.

bulk plant—A bulk plant is a distributing unit for petroleum products usually having car-load unloading facilities for light oils on railroad sidings. It has aboveground storage for one or more car loads of light oils and a warehouse with storage for petroleum products sold in barrels or packages.

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[2] Not taken from API Manual "Glossary of Terms Used in Petroleum Refining."

bunker "C" fuel oil—A heavy residual fuel oil used by ships, industry, and for large-scale heating installations.

C

casinghead gasoline—The liquid hydrocarbon product extracted from natural gas.

charge—A quantity of feed stock for a refinery processing unit.

coke drum—A vessel in which coke is formed and which can be cut off from the process for cleaning.

coking—The process of distilling a petroleum product to dryness. The undesirable building up of coke or carbon deposits on refinery equipment.

combination cracking—A process involving crude distillation, viscosity breaking, naphtha reforming, and gas-oil cracking, and one which in the extreme might also involve gas recovery and even coking.

cooker—A lead-lined vat or tank in which acid sludge resulting from chemical treatment of lubricating oils is subjected to agitation for recovery of acid. These vats are used also for mixing the acid sludge from light distillates with water.

cooling tower—A unit or structure, usually built of wood, for the purpose of cooling water by evaporation.

cracked fuels—Fuels consisting predominantly of cracked residuum which may or may not be blended with cracked distillate.

cracked gases—The gases resulting from the breaking down or cracking of petroleum oils.

cracking—Cracking is a phenomenon by which large oil molecules are decomposed into smaller lower-boiling molecules; at the same time certain of these molecules, which are reactive, combine with one another to give even larger molecules than those in the original stock. The more stable molecules leave the system as cracked gasoline, but the reactive ones polymerize, forming tar and even coke.

crude still—A piece of refinery equipment designed to permit physical separation of crude oil by the application of heat.

cuts—Petroleum fractions obtained in the distillation of oil.

cycle stock—Product taken from some later stage of a process and recharged to the process at some earlier stage.

cylinder stock—The residuum remaining in a still after the lighter parts of a crude have been vaporized.

D

dehydrogenation—The removal of hydrogen from a chemical compound.

destructive distillation—A process of distillation in which an organic compound or mixture is heated to a temperature high enough to cause decomposition.

diolefins—Open-chain hydrocarbons having two double bonds per molecule. The empirical formula is C_nH_{2n-2}. They have been shown to be particularly conducive to oxidation, gum formation, and loss of octane rating on storage. They are readily removed from cracked naphthas by clay or acid treating.

distillate—The product of distillation obtained by condensing the vapors from a still.

doctor test—A qualitative method of detecting undesirable sulfur compounds in petroleum distillates, i.e., of determining whether an oil is "sour" or "sweet."

doctor treatment—Treatment of gasoline with sodium-plumbite solution and sulfur to improve its odor.

dopes for gasolines—Materials added in small amounts to gasoline to increase the octane number and thus help to prevent knocking. Tetraethyllead is the most common dope used.

drum, flash—A drum or tower into which the heated outlet products of a preheater or exchanger system are conducted, often with some release in pressure. The purpose of the drum is to allow vaporization and separation of the volatile portions for fractionation elsewhere.

dry gas—A gas which does not contain the heavier fractions which may easily condense under normal atmospheric conditions. In the hydrocarbon series, methane and ethane, for example, are dry gases.

E

engine distillate—Refined or unrefined petroleum distillate similar to naphtha but often of higher distillation range.

evaporator—Usually a vessel which receives the hot discharge from a heating coil and, by a reduction in pressure, flashes off overhead the light products and allows the heavy residue to collect in the bottom.

F

fixed gas—Gas which will not condense under pressure and temperature conditions available in the process under consideration.

flashing—Effecting a separation of products by releasing the pressure on a hot oil as it enters a vessel; the lighter fractions vaporize or "flash" off and heavy oil drops to the bottom.

floating roof—A special tank roof which floats upon the oil.

fractional distillation—The separation of the components of a liquid mixture by vaporizing and collecting the fractions which condense in different temperature ranges.

furnace oil—A distillate fuel primarily intended for domestic heating use. No. 1 commercial standard grade is intended for "vaporizing" burners requiring a volatile fuel, whereas Nos. 2 and 3 commercial standard grades are less volatile, are usable in the "atomizing" type of burners and, also, generally are cheaper.

G

gas oil—A liquid petroleum distillate with a viscosity and boiling range between kerosine and lubricating oil.

gum—In the petroleum industry, the term is descriptive of rosin-like insoluble deposits formed during the deterioration of petroleum and its products, particularly gasoline.

H

heart-cut—A narrow-range "cut" usually taken near the middle portion of the stock being distilled or treated.

heavy ends—The highest-boiling portion present.

hydrocarbon—A compound containing only hydrogen and carbon. The simplest hydrocarbons are gases at ordinary temperatures, but with increasing molecular weight they change to the liquid form and finally to the solid state. They form the principal constituents of petroleum.

hydrogenation—The chemical addition of hydrogen to a material.

I

ibp—Initial boiling point.

innage—Converse of outage; refers either to the volume of liquid or the measured height of liquid in a tank or container, as measured from the bottom of the tank.

isomate—Product obtained as a result of isomerizing a straight-run low-boiling naphtha.

isomerization—Process for altering the fundamental arrangement of the atoms in the molecule without adding or removing anything from the original material.

K

knockout drum—A drum or vessel constructed with baffles through which a mixture of gas and liquid is passed to disengage one from the other. As the mixture comes in contact with the baffles, the impact frees the gases and allows them to pass overhead; the heavier substance falls to the bottom of the drum.

L

lead susceptibility—Ability of gasoline to respond to the addition of tetraethyllead as reflected in the increase in anti-knock quality per increment of lead added.

lean oil—Absorption oil from which natural-gasoline fractions have been removed. Oil leaving the stripper in a natural-gasoline plant.

light ends—The lower-boiling components of a mixture of hydrocarbons.

LPG—Industry initials for certain liquefied petroleum gases. These are hydrocarbon fractions lighter than gasoline, such as butane, propane, etc., which are kept under pressure in a liquid state and marketed for various industrial and domestic gas uses.

M

manifold—A piping arrangement which allows one stream of liquid or gas to be divided into two or more streams, as the manifold of an automobile engine.

M c.f.—The abbreviation for "thousands of cubic feet."

mercaptans—Organic compounds having the general formula R—SH, meaning that the thiol group, —SH, is attached to a radical such as CH_3 or C_2H_5, etc. The simpler mercaptans have strong, repulsive, garlic-like odors which become less pronounced with increasing molecular weight and higher boiling points.

N

natural gas—Gaseous forms of petroleum, commonly called "natural gas," consist of mixtures of hydrocarbon gases and vapors, the more important of which are methane, ethane, propane, butane, pentane, and hexane, all of the paraffin series (C_nH_{2n+2}).

O

olefins—Open-chain hydrocarbons having one or more double bonds per molecule; specifically, hydrocarbons belonging to the monoolefin or ethylene series (C_nH_{2n}) having one double bond per molecule (as compared with diolefin, triolefin, etc.).

oleum spirits—A petroleum cut, boiling between 300° and 400° F., meeting certain other specifications.

onstream time—The length of time a unit is in actual production.

operating efficiency—The percentage of the time during which a unit is performing its function; e.g., if a unit runs 800 hours (onstream time), takes 100 hours for reconditioning and inspection, and 100 hours for starting up and shutting down, the operating efficiency would be 80 percent.

outage—The difference between the full or the rated capacity and the actual contents of a barrel, tank, or tank car. The vertical distance between the surface of the liquid in a barrel, tank, or tank car, and the top of the container.

overhead—In a distilling operation, that portion of the charge which is vaporized.

P

pipe still—Still in which heat is applied to the oil while being pumped through a coil or pipe arranged in a suitable firebox. After leaving the heating zone, the pipe runs to a fractionator where a portion of oil is taken off overhead as vapor, and the liquid portion removed continuously.

polymerization—The process of combining two or more molecules to form a single molecule having the same elements in the same proportions as in the original molecules. Specifically, in the petroleum industry, the union of light olefins to form hydrocarbons of higher molecular weight.

pressure distillate—The light, gasoline-bearing distillate product from the pressure stills which has been produced by cracking, as contrasted with virgin or straight-run stock.

pump, reciprocating—A positive-displacement type of pump consisting of a plunger or a piston moving back and forth within a cylinder. With each stroke of the plunger or piston, a definite volume of liquid is pushed out through the discharge valves.

R

reboiler—An auxiliary of a fractionating tower designed to supply additional heat to the lower portion. Liquid is usually withdrawn (or pumped) from the side or bottom of the tower; is reheated by means of heat exchange; and the vapors and residual liquid, separately or together, are re-introduced to the tower.

reducing—In petroleum refining, the removal of light hydrocarbons by distillation.

refinery gas—Any form or mixture of still gas gathered in a refinery from the various stills.

reflux—In fractional distillation, part of the distillate may be returned to the fractionating column to assist in making a more complete separation into the desired fractions. The material returned is the reflux; the process is refluxing.

regeneration—In a catalytic process, the burning of the catalyst deposit with an oxygen-containing gas.

Reid vapor pressure—One of the important specifications for gasolines. It is a measure of the vapor pressure of a sample at 100° F., and the test is commonly made in a bomb. The results are reported in pounds per square inch.

rerun oil—Oil which has been redistilled.

residual—Heavy oil or residuum left in the still after gasoline and other distillates have been distilled off, or residue from crude oil after distilling off all but the heaviest components.

rich oil—Absorption oil containing dissolved natural-gasoline fractions.

run—The amount of stock processed by a particular unit in a given time. It is often used colloquially in relation to the type of stock being processed.

Rvp—Reid vapor pressure.

S

saturated hydrocarbons—Hydrocarbons of such molecular structure that all adjacent carbon atoms are connected by not more than one valence or bond, or graphically, as follows: C—C. Each valence not taken up by adjacent carbon atoms connects with, or is satisfied by, a hydrogen atom. These compounds cannot take on other products or the atoms of other elements without giving up an equivalent amount of hydrogen.

scrubber—Equipment used for the removal of entrained liquids and solids from gas, usually installed upstream from gas compressors.

skimming plant—An oil refinery designed to remove and finish only the lighter constituents from the crude oil, such as gasoline and kerosine. In such a plant the portion of the crude remaining after the above products are removed is usually sold as fuel oil.

slop or slop oil—A term rather loosely used to denote odds and ends of oil produced at various places in the plant, which must be rerun or further processed in order to get in suitable condition for use. When good for nothing else, such oil usually goes into pressure-still charging stock, or to coke stills.

sour—Gasolines, naphthas, and refined oils are said to be "sour" if they show a positive "doctor test," i.e., contain hydrogen sulfide and/or mercaptans. Sourness is directly connected with odor, while a "sweet" gasoline has a good odor.

stabilizer—A distilling plant in which "wild" or low-boiling hydrocarbons (which have high vapor pressure) are removed from pressure distillate or gasoline.

steam distillation—Introduction of "open" steam into the liquid during distillation to assist in removing the vapors from the still.

still—A closed chamber, usually cylindrical, in which heat is applied to a substance to change it into vapor, with or without chemical decomposition. The substance, in its vapor form, is conducted to some cooling apparatus where it is condensed, liquefied, and collected in another part of the unit to which the still belongs.

stock—In general, any oil which is to receive further treatment before going into finished products.

straight-run distillation—Continuous distillation which separates the products of petroleum in the order of their boiling points without cracking.

straight-run products—Products produced by straight-run distillation.

stripper—Equipment in which the lightest fractions are removed from a mixture. In a natural-gasoline plant, gasoline fractions are stripped from rich oil. In the distillation of crude petroleum, light fractions are stripped from the various products.

sweet—Having a good odor; pleasant to the sense of smell; negative to the "doctor test."

sweetening—The process by which petroleum products are improved in odor and color by oxidizing the sulfur products and unsaturated compounds.

synthetic crude—The total, liquid, multi-component mixture resulting from a process involving molecular rearrangement of charge stock. Commonly applied to such product from cracking, reforming, visbreaking, etc.

T

tail—That portion of an oil which vaporizes near the end of the distillation; the heavy end.

tank farm—Land on which a number of storage tanks are located.

topped crude petroleum—A residual product remaining after the removal, by distillation or other artificial means, of an appreciable quantity of the more volatile components of crude petroleum.

topping—The distillation of crude oil to remove light fractions only.

turnaround—Time necessary to clean and make minor repairs on refinery equipment after a normal run. It is the elapsed time between drawing the fires (shutting the unit down) and putting the unit onstream again.

U

unsaturated hydrocarbons—Hydrocarbons of such molecular structure that at least two adjacent carbon atoms are connected by two or three valences or bonds, or graphically, as follows: $C{=}C$ or $C{\equiv}C$. Each valence not taken up by an adjacent carbon atom is satisfied by a hydrogen atom.

V

vacuum distillation—Distillation under reduced pressure. The boiling temperature is thereby reduced sufficiently to prevent decomposition or cracking of the material being distilled.

vacuum jets—Steam ejectors for removing air and non-condensable gases from barometric condensers on distillation equipment.

virgin stock—Oil derived directly from crude oil which contains no cracked material. Also called "straight-run" stock.

viscosity breaking—Lowering or "breaking" the viscosity of residuum by cracking at relatively low temperatures.

W

weathered crude—The product resulting from crude petroleum through loss, due to natural causes during storage and handling, of an appreciable quantity of the more volatile components.

wet gas—A gas containing a relatively high proportion of hydrocarbons recoverable as liquids.

Y

yield—The percentage of specification material obtained in distilling, extracting, etc.

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